PHASE AND PARTITIONING BEHAVIOR OF PHENOLS AND POLYCYCLIC AROMATIC HYDROCARBONS IN OFFSHORE OIL AND GAS PRODUCED WATER

By

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ABSTRACT

Produced water constitutes the largest volume of waste from offshore oil and gas operations and is composed of a wide range of organic and inorganic compounds. Although treatment processes have to meet strict oil in water regulations, the definition of "oil" is a function of the analysis process and may include aliphatic hydrocarbons which have limited environmental impact due to degradability whilst ignoring problematic dissolved petroleum species. This thesis presents the partitioning behavior of oil in produced water as a function of temperature and salinity to identify compounds of environmental concern. Phenol, p-cresol, and 4-tert-butylphenol were studied because of their xenoestrogenic power; other compounds studied are polycyclic aromatic hydrocarbon PAHs which include naphthalene, fluorene, phenanthrene, and pyrene. Partitioning experiments were carried out in an Innova incubator for 48 hours, temperature was varied from 4^{o}C to 70^{o}C, and two salinity levels of 46.8‰ and 66.8‰ were studied. Results obtained showed that the dispersed oil concentration in the water reduces with settling time and equilibrium was attained at 48 h settling time. Polycyclic aromatic hydrocarbons (PAHs) partitions based on dispersed oil concentration whereas phenols are not significantly affected by dispersed oil concentration. Higher temperature favors partitioning of PAHs into the water phase. Salinity has negligible effect on partitioning pattern of phenols and PAHs studied. Simulation results obtained from the Aspen HYSYS model shows that temperature and oil droplet distribution greatly influences the efficiency of produced water treatment system.

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List of Symbols, Nomenclature and Abbreviations

ACS	America Chemical Society
BTEX	Benzene toluene ethylbenzene xylene
DCCLC	Dynamic Coupled Column Liquid Chromatography
DCM	Dichloromethane
DREAM	Dose-Related Risk and Effect Assessment Model
EIF	Environmental Impact Factor
GC-MS	Gas Chromatography – Mass Spectrometer
K-D	Kuderna-Danish
MF	Microfiltration
MPPE	Macro Porous Polymer Extraction
NF	Nano-Filtration
NIST	National Institute of Standards and Technology
NPD	Naphthalene phenanthrene dibezothiophene
OGP	Oil and Gas Producer
PAH	Polycyclic Aromatic Hydrocarbon
PPT	Part per thousand
RO	Reverse Osmosis
SIM	Selected Ion Monitoring
TBP	True Boiling Point
TEOCs	Total Extractable Organic Compounds
TPH	Total Petroleum Hydrocarbon

UF	Ultra-Filtration
WAF	Water Accommodated Fraction
WOR	Water to Oil Ratio
WSF	Water Soluble Components
C_i	Concentration of component *i*
$C_{iw}^{sat}(L)$	Concentration in the aqueous phase (mol/L)
$C_i^{w,T}$	Total (observed) aqueous concentration (mol/L)
$C_i^{w,s}$	Aqueous solubility (mol/l)
$C_{iw}^{sat}(salt)$	Corrected solubility for salinity (mol/L)
C_i	Dispersed oil concentration in the water inlet stream (mg/L)
C	Dispersed oil concentration in the water outlet stream (mg/L)
C_o	Equilibrium concentration in the octanol (mg/L)
C_w	Equilibrium concentration in the water phase (mg/L)
C_{wo}	Concentration of the component in the aqueous phase (mg/L)
D	Diameter of pipe (mm),
d	Oil droplet diameter (μm)
E_{ff}	Oil removal efficiency (%)
g	Acceleration due to gravity (m/s^2)
H_{iw}^E	Contribution to the excess free energy
K	Oil-water partition coefficient,
k_{is}	Salting out constant,

K_{ow}	Octanol/water partitioning coefficient
L	Pipe length (m)
m	Total mass flow rate of fluid (kg/h)
P	Pressure (kPa)
Q	Volumetric flow rate (m^3/h)
R	Gas constant ($J\ K^{-1}\ mol^{-1}$)
T	Temperature (^oC)
v^o	Average molar volume of oil (l oil/l mol oil),
X_i^o	Mole fraction of component i in the oil
x_i	Mass fraction of component i
Φ^o	Volume fraction oil emulsion in water (l emulsion/l water),
ρ_o	Density of oil (kg/m^3)
ρ_w	Density of water (kg/m^3)
V_r	Rising velocity of the oil (m/s)
Vt	Total volumetric flow rate of fluid (m3/h)
μ	Viscosity of fluid (Pa.s)

Chapter 1: Introduction and Overview

1.1 Introduction

Input of oil to sea comes from various sources which include: natural seeps, marine transportation (pipeline spills, tank vessel spills, cargo washing, coastal facility spills), bilge pumping from ships, produced waters, and consumption of petroleum products. Produced water is the largest offshore discharge associated with oil and gas production [1].

Typically, oil and gas reservoirs have a natural water layer (called formation water) associated with the petroleum. Oil reservoirs frequently contain large volumes of water, while gas reservoirs contain smaller quantities [2]. Additional water, such as seawater, may be injected to the reservoir to enhance oil recovery, thereby, increasing the water recovered with the oil/gas. At the surface, the water is separated from the oil and the water is referred to as produced water. Produced water is treated to remove residual oil, and then discharged into the sea and/or injected back into the wells. As an oil field becomes depleted, the amount of produced water increases as the reservoir ages [3]. Because the water has been in contact with hydrocarbon-bearing formations, it contains some of the chemical characteristics of the formations and the hydrocarbons. It may include water from the reservoir, water previously injected into the formation, and any chemicals added during the production processes. The physical and chemical properties of produced water vary considerably depending on the geographic location of the field,

the geologic formation, and the type of hydrocarbon product being produced either gas or oil [2]. Produced water properties and volume also vary throughout the lifetime of a reservoir [1].

In most fields, the volume of water produced is far more than the oil recovered. Typical water to oil ratio (WOR) of 2:1 to 3:1 have been estimated worldwide [1]. The WOR also increases as the reservoir ages. There is no way to accurately estimate worldwide discharged produced water volume due to unavailability of figures from certain regions. Khatib and Verbeek (2003) estimated global produced water to be 12.24 billion m^3/yr [4]. The volume of produced water from Norwegian offshore oil activities was estimated to be 172.46 million m^3 in 2014 [5]. In offshore Newfoundland and Labrador, the three producing fields produced a total of 15.86 million m^3 in 2014 [6]. Treatment of produced water is not straight forward and becomes especially challenging in remote offshore locations where space and operational infrastructure is limited. There is no single treatment technology that can effectively remove all the contaminants of environmental concern from produced water [7, 8]. Cold temperature, limited space and high motion make in situ analysis and control difficult.

1.2 Scope and Objectives

The objective of this research is to determine the phase and partitioning behavior of contaminants considered of great environmental concern in offshore oil and gas produced water between the oil and water phase.

This thesis will cover the following areas:

- Relationship between dispersed oil concentration and concentration of target analytes (phenol, p-cresol, 4-tert-butylphenol, naphthalene, fluorene, phenanthrene, and pyrene) in produced water.
- Effect of temperature on the partitioning behavior of target analytes in offshore oil and gas produced water between the oil phase and water phase.
- Effect of salinity on the partitioning behavior of target analytes in offshore oil and gas produced water.
- Steady state modeling of produced water treatment system using Aspen HYSYS version 8.6 to remove oil in produced water. Analysis will focus on the partitioning behavior of phenol, p-cresol, naphthalene, fluorene, phenanthrene, and pyrene in produced water.
- Comparism of experimental results with HYSYS simulated results.

1.3 Organization

The background of the study is presented in Chapter 1. A literature review is presented in Chapter 2 which provides details on the produced water; composition, compounds of environmental concern, partitioning pattern and factors that influence partitioning, fate in the marine environment, and management options. Experimental methodology and model development is described in Chapter 3. Chapter 4 presents experiment results and comparison with data available in literature. Chapter 5 presents modeling and simulation

of produced water treatment system, simulation result and comparison of simulation result and experimental result.

Chapter 6 summarizes the research findings and recommendations for future research scope.

Chapter 2: Literature review

2.1 Produced water composition

Produced water composition is dependent on the field geology, the degree of treatment, production methods, and age of the reservoir. The waters contains both dispersed oil and dissolved hydrocarbons, organic acids, metals, phenols, alkylated phenols and trace of chemicals added in the separation and production line [9]. Aliphatics make up the bulk of the dispersed phase which form small droplets of oil suspended in the water phase. Upon discharge, dispersed oil may contact the ocean floor and contaminate/accumulate on the ocean sediment [10]. Dispersed oil may also form a sheen of oil on the water surface thereby increasing the biological oxygen demand close to the point of discharge [2]. Dissolved hydrocarbons are dominated by the volatile aromatic fraction of the oil, namely benzene, toluene, ethylbenzene and xylene (BTEX). The polycyclic aromatic hydrocarbons (PAHs) are dominated by naphthalene, phenanthrene and dibenzothiophene (NPD) and their C1-C3 alkyl homologues. Also compounds with higher molecular weight are reported, such as pyrene, chrysene and benzo[a]pyrene [9]. Phenols are also ubiquitous and can consist of long alkyl groups in produced water [11]. While organic acids are dominated by C1-C6 acids. Utvik et al. (2002) summarized the composition of produced water in (Table 2.1)

Table 2.1: Chemical composition of produced water from main sources in the Norwegian sector of the North Sea 1999-2000. Source [11]

Compound group	**Low**	**High**
Dispersed oil mg/L	10	40
BTEX mg/L	1	40
NPD mg/L	0.9	10
PAH mg/L	0.010	0.13
Organic acids mg/L	55	760
Phenol mg/L	0.1	6
C1-C4 alkylated phenols mg/L	0.170	11.3
C4-C7 alkylated phenols mg/L	0.1	0.8
Radioactive elements Bq/L	0.1	10

The most common organic acids in produced water are carboxylic acids and sulfonic acids containing $–SO_2OH$ [9]. The most abundant in produced water are fatty acids, which are long unbranched aliphatic molecules with a carboxyl group (COOH), e.g. acetic acid (CH_3COOH) [7]**.** Phenol is soluble in water (83g/mL) and is mildly acidic. Phenols can be alkylated to form alkylphenols (phenols with an alkyl group), the higher the alkylation the less water soluble it becomes [12]. Alkyl phenols play a crucial role in the xenoestrogenic potency of produced water [11, 13]. The endocrine disruptive capability of phenols increases with degree of alkylation [7, 11, 12]. The focus of this study will be on the dispersed and dissolved oil fraction with emphasis on those compounds that are considered problematic in the environment due to their toxicity or persistence. Meijer et al., 2007 [8] identified: aromatics (PAH), phenols, and alkyl-phenols as toxic, carcinogenic, mutagenic and less biodegradable components of

produced water [14]. Others are the chemicals which are added in the production and separation processes. These chemicals include: corrosion inhibitors and oxygen scavengers to reduce equipment corrosion; scale inhibitors to reduce deposit of salts and minerals along pipeline and equipment; coagulants, flocculants, and clarifiers to remove solids; emulsion breakers to break down oil-water emulsions and solvents to reduce paraffin deposition [2].

2.2 Partitioning of Produced Water (Dissolved vs. Dispersed)

The hydrocarbons in produced water can be broadly categorized into polar and non-polar hydrocarbons and partition into dispersed or dissolved phase. While the non-polar aliphatic exist mostly in the dispersed phase and tend to float, the polar hydrocarbons tend to dissolve [8]. Carboxylic acids are generally water soluble [7]. According to Faksness et al. (2004) [12], the concentration C4+ (having four or more benzene rings) PAHs and C6+ alkylated phenols (having one or more alkyl group with more than six carbons attached to the parent) in produced water correlates directly with dispersed oil concentration [12]. At a concentration of 20 mg/L of dispersed oil, about 10% naphthalene and 70% C3 naphthalene were in the dispersed oil [12]. Similarly, 40% of 4-n-pentylphenol was associated with dispersed oil at 20 mg/L of dispersed oil concentration in produced water as shown in Figure 2.1. BTEX and C0-C3 alkylated phenols are soluble in water [12]. Naphthalene and methyl-naphthalene have relatively high solubility in water compared to ethyl and higher substituted (C2+) naphthalene.

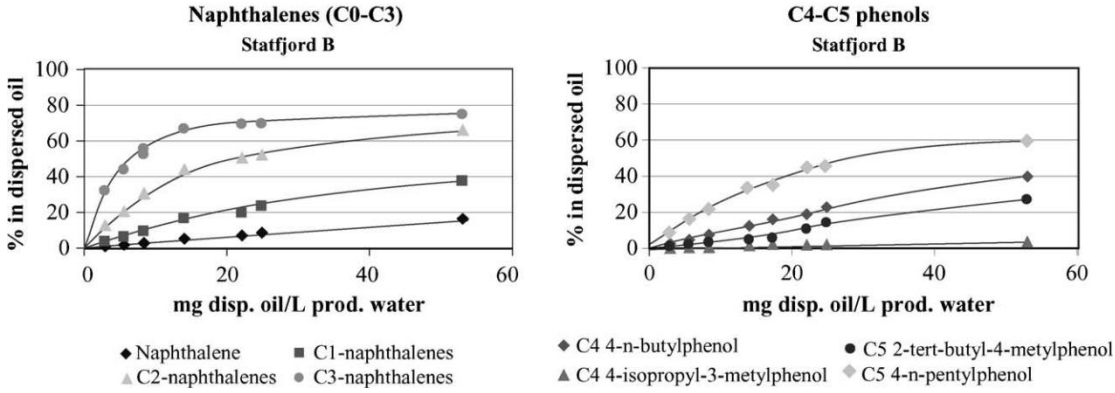

Figure 2.1: Distribution of naphthalene it's alkyl homologues and C4 & C5 phenols in settling experiments. Reproduced from ref [12]

The water solubility of the components within both the group of naphthalenes and the group of butyl and higher phenol varies depending on the degree of alkylation [12]. Soluble fractions of produced water are not easily removed by conventional treatment processes and are usually discharged to the ocean. The bioavailability of these compounds makes them a possible contaminant of concern, depending on the energy and conditions of the receiving environment, and the concentration in the produced water.

Prior to the introduction of the Environmental impact factor (EIF) by the Norwegian oil Industry, the chemical characterization of produced water was been limited to measurement of dispersed oil [13]. The EIF calculation is based on the environmental risk and hazard assessment, which considered four factors: produced water dilution and dispersion describing the environmental concentration (PEC); risk assessment (Dose-related risk and effect assessment model DREAM); water volumes; and additional weightings to account for bioaccumulation and food chain transfer. Utvik et al. (2002)

[13] proposed compounds in produced water which are problematic in the marine environment in Table 2.2

Table 2.2: Produced water compounds included in the calculations of environmental impact factor (EIF) [13]

Main group	Compounds	Representative compound
BTEX	Benzene, toluene, ethyl-benzene, xylene	Ethyl-benzene
Naphthalene	Naphthalene + C1-C3 alkyl homologues	Naphthalene
PAH 2-3 ring	Compounds on the EPA 16 PAH list with 2-3 rings	Phenanthrene
PAH 4-ring +	Compounds on the EPA 16 PAH list with 4 rings or more	Chrysene
Alkyl-phenols C0-C3	Phenol + C1-C3 alkyl-homologues	p-Cresol
Alkyl-phenols C4+	C4-phenol and higher alkyl-homologues	Nonylphenol
Aliphatic	"dispersed oil" as defined by analytical method	-
Hydrocarbons		
Metals	Zn, Cu, Ni, Hg, Cd, Pb	Field-specific
Scale inhibitor	Field-specific	Field-specific
Defoamer	Field-specific	Field-specific
Emulsion breaker	Field-specific	Field-specific
Corrosion inhibitor	Field-specific	Field-specific

2.3 Partitioning of Compounds of environmental Concern between the water phase and oil phase

In order to determine a compounds' particular EIF it is necessary to understand the partitioning behavior between gas, water, and oil phases. The partition coefficient (K) is a measure of the solubility of a compound in two immiscible phases. The octanol/water

partition coefficient (K_{ow}) is frequently used to measure the partitioning of contaminants between oil and water.

$$K_{ow} = \frac{C_o}{C_w}. \qquad (2.1)$$

Where; C_o is the equilibrium concentration in the octanol, C_w is the equilibrium concentration in the water phase. It is usually expressed as log K_{ow}. A typical value of log K_{ow} less than 4 (K_{ow}<10,000) indicates solubility in the water phase is significant [7]. Table 3 summarizes the log K_{ow} for PAHs of interest in produced water. From the log K_{ow} presented in table 2.3 in an octanol/water system, solubility in the water phase is favored for phenols, naphthalene and C1 naphthalene. While phenanthrenes, dibenzothiophenes, and higher PAHs are less soluble in water and are predominantly in the octanol phase.

Table 2.3: Log K_{ow} of selected compounds in produced water at 25 ^{o}C

Compound	**Log K_{ow}**
Phenols	
Phenol	1.46[a]
p-cresol	1.97[a]
4-tert-butylphenol	3.04[a]
NPD	
Naphthalene	3.37
C_1 – Naphthalene	3.87
C_2 – Naphthalene	4.37
C_3 – Naphthalene	5.00
Phenanthrene	4.57
C_1 Phenanthrene	5.14
C_2 Phenanthrene	5.51
C_3 Phenanthrene	6.00
Dibenzothiophene	4.49
C_1 Dibenzothiophene	4.86

C_2 Dibenzothiophene	5.50
C_3 Dibenzothiophene	5.73
PAH	
Acenaphthylene	4.07
Fluorene	4.18
Anthracene	5.22
Fluoranthene	5.22
Pyrene	5.18
Benz(a)anthracene	5.91
Chrysene	5.86
Benzo(b)fluoranthene	5.8
Benzo(k)fluoranthene	6.00
Benzo(a)pyrene	6.04
Benzo(ghi)perylene	6.50

[a]values from reference [15]

Although several works in the literature have been done on partitioning organic compounds between water and octanol phases, few have attempted to study how organic compounds partition between the water phase and dispersed oil phase. In 2004, Faksness et al. conducted a series of experiments to study the partitioning behavior of compounds (included in the calculation of EIF) between the oil phase and water phase in produced water. A relation between the dispersed oil concentration and various compounds in the EIF groups was developed [12]. The study was carried out at ambient temperature, where dispersed oil in produced water was allowed to settle to the surface thereby partitioning between the oil phase and aqueous phase over a 48 hours period. The concentrations of the EIF groups were measured as the dispersed oil settled to the surface (Table 2.4)

Table 2.4: Concentration of EIF components in produced water at various concentrations of dispersed oil [12]

Dispersed oil	**40 mg/L**	**20 mg/L (50% reduction)**		**5 mg/L (87.5% reduction)**	
EIF groups	µg/L	µg/L	%Reduction	µg/L	%Reduction
Naphthalenes	1201	855	29	596	50
2–3 Ring PAH	167	85.8	49	24.8	85
4–6 Ring PAH	3.22	1.61	50	0.4	88
C0–C3 phenols[a]	4303	4125	None[b]	3991	None[b]
C4–C5-phenols[a]	182	162	11	148	19
C6–C9-phenols	2.95	1.79	39	0.92	69

[a]Total ion chromagram integrated. [b]Insignificant reduction (due to analytical variation).

From Table 2.4, there is no significant reduction in the concentration of C0–C3 Phenols as the concentration of dispersed oil is reduced from 40 mg/L to 5 mg/L, this is not unexpected given the K_{OW} of phenols in these temperature ranges (e.g. phenol at 15^{o}C has a K_{OW} of 28.84) . Conversely, as dispersed oil concentration was reduced from 40 mg/L to 5 mg/L, naphthalene and 2–3 Ring PAHs reduced by 50% and 85% respectively. Similarly, 4-6 ring PAHs was also reduced by 88% as dispersed oil concentration is reduced from 40 mg/L to 5 mg/L. Although, the concentration of 4-6 rings PAHs is relatively small at 40 mg/L of dispersed oil in produced water, it constitutes the highest risk to environment impact as shown in figure 2.2. At 5 mg/L of dispersed oil concentration, the contribution of PAHs to EIF is drastically reduced while the contributions from Phenols are relatively unchanged. It can be inferred that the concentrations of PAHs are strongly correlated to disperse oil concentration. Therefore, produced water treatment option that reduces dispersed oil also reduces concentration of

PAHs to a large extent. Phenols are not significantly impacted by dispersed oil concentration. The solubility of PAHs also decreases with an increasing number of rings. This work clearly demonstration how these compounds partition between the aqueous phase and oil phase.

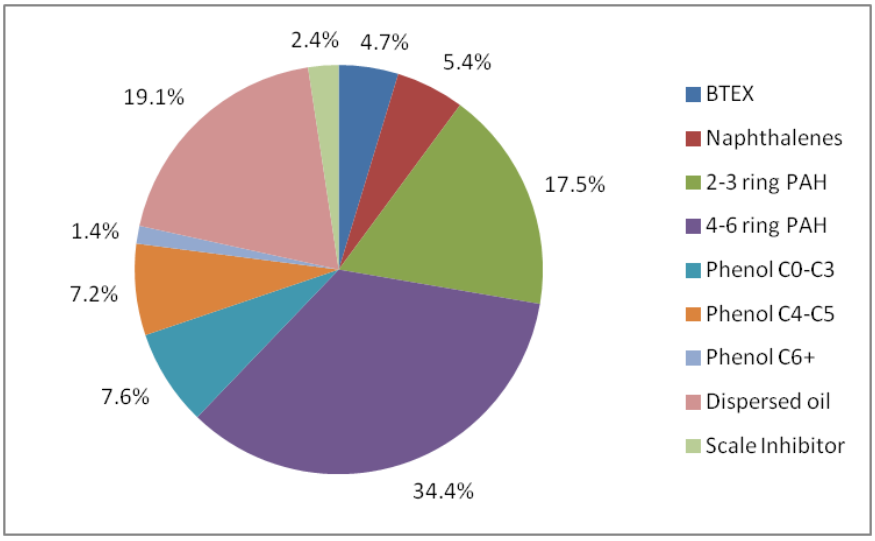

Figure 2.2: The contribution to environmental risk (EIF) from the different component groups when the dispersed oil concentration in the produced water is 40 mg/L [12].

The impact of temperature and salinity on partitioning behavior of compounds in produced water are not well studied. This extends to conditions typical in Arctic locations, where cold temperature are likely to impact the efficiency of produced water treatment systems [7] . However, a sizeable number of studies have been carried out on water solubility of components crude oil and petroleum products [14, 16, 17].

In 2008, Faksness et al. conducted another series of experiments in the laboratory to study the composition of water accommodation fraction (WAF) in sea water. The study validated that it takes a longer for the WAF to reach equilibrium at low temperatures (2

^{o}C) compare to WAF at 13 ^{o}C [14]. Furthermore, it takes less time for paraffinic oil to reach equilibrium concentrations in the aqueous phase compared to waxy oils. The composition of WAF was also found to be different from the parent crude oil. Similar experiments were carried out by Page et al in 2000 [17]. Two sets of experiments were conducted to determine the controlling mechanism governing the aqueous concentrations of naphthalene and its derivatives in oil/water reactor systems. The first experiment was carried out at oil to water ratio of 1:10. The results obtained shows that equilibrium concentration of naphthalenes was achieved after a 24 hour period (indicated by the arrow) as shown in Figure 2.3.

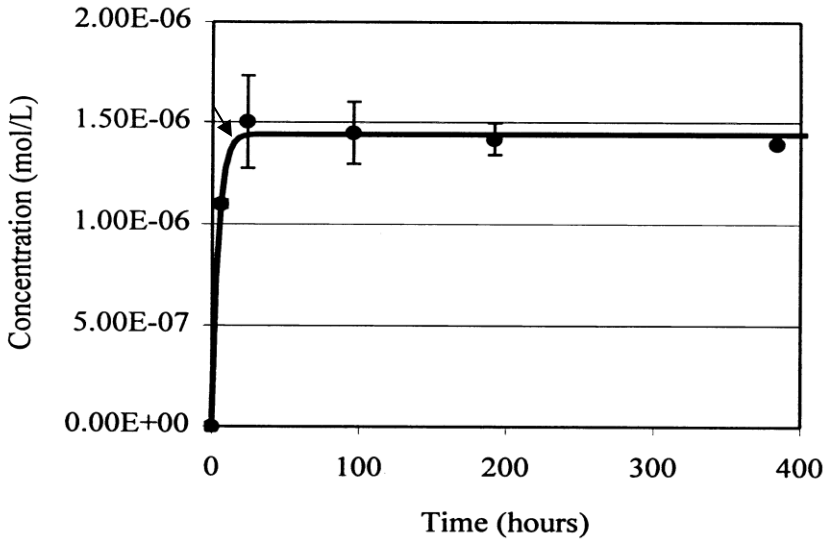

Figure 2.3: Aqueous concentration of naphthalene over time [17].

(Model results is represented by the curve while the data point with error bars shows experiment results)

Modeled results were found to be in good agreement with the experiments results. The saturation kinetic model used was as outlined below:

$$\frac{dC}{dt} = k(C^* - C) \tag{2.2}$$

Where C* is the saturation concentration of the compound (mol/L), C is the time-variable concentration of the compound, k is the first-order rate constant (h^{-1}). Page et al. also demonstrated the solubility decrease with increasing degree of alkylation in a second set of experiments. The oil loading was varied and the TPH varied proportionally with the oil loading. However, there is no correlation found between oil loading and concentration of naphthalenes, C1-naphthalenes, and C2- naphthalenes. The only explanation put forward was the presence of micro-droplets of oil in the aqueous phase. If this happens, the total observed aqueous concentration of component i was given as,

$$C_i^{w,T} = \frac{\Phi^o X_i^o}{v^o} + X_i^o C_i^{w,s}. \tag{2.3}$$

Where, $C_i^{w,T}$ = total (observed) aqueous concentration (mol/L), Φ^o = volume fraction oil emulsion in water (l emulsion/l water), X_i^o = mole fraction of component I in the oil, v^o = average molar volume of oil (l oil/l mol oil), $C_i^{w,s}$ = aqueous solubility (mol/l).

Contribution from the oil is the first term of equation 2.3, while the second term represents solubility in the aqueous phase. The second term represents Raoult's law and can be evaluated if the mole fraction of the component in the oil is known. This explains why reported concentrations in saturated WAF are significantly lower than published aqueous solubility [18] values. From equation 2.3 above, the observed aqueous concentration of a compound depends on the following: volume fraction of oil emulsion in water; mole fraction of the compound in the oil; average molar volume of oil; and the

aqueous solubility of the compound. Therefore, the observed aqueous concentration of a compound in oil/water system weakly depends on the aqueous solubility of the pure compound. Furthermore, crude oil contains hundreds of compounds which make the estimation of mole fraction of a compound difficult.

Shiu et al. (1990) [16] studied the water solubility of several crude oils and petroleum products in double distilled water and also in 3% NaCl solution. Oil was added to 50-100 mL of water in a 125 mL separatory funnel. Various oil loadings (maximum oil loading of 1:40) were tested for 42 oil types including weathered and fresh oils. Stirring was carried out for a minimum period of 24 h with a wrist action shaker or magnetic stirrer without generating oil-in-water emulsion. The set up was then placed in a temperature controlled bath for another 48 h before analysis. Results obtained show that water solubility of crude oil and petroleum products greatly reduced from fresh oil to weathered oils across all oil types as the majority of the water soluble fraction was lost during the weathering process. Benzene, toluene, ethylbenzene, xylene, and naphthalene were the major components of water soluble fraction (WSF) of crude oil at 20-25 ^{o}C [16]. Generally, WOR used in this experiment significantly influences the composition and concentration of WSF in the aqueous phase. The total concentration of WSF in the aqueous phase reduces with increasing WOR. However, the observed concentration of naphthalene in the aqueous phase is relatively unchanged. A simplified mass balance (equation 2.4) proposed by Shiu et al (1990) [16] was employed to estimate the partitioning coefficient based on the concentration of components in the water phase.

$$C_w = \frac{C_{wo}}{1 + Q/K}. \quad (2.4)$$

Where C_w = concentration of any component in the aqueous phase, K = oil-water partition coefficient, Q = water to oil volume ratio, and C_{wo} = concentration of the component in the aqueous phase at Q equals zero. C_{wo} was determined by extrapolating the concentration to a zero water-to-oil ratio. From the relation above, it can be deduced that the concentration of soluble compounds with low partitioning coefficient are more sensitive to the oil loading. The oil-water partitioning coefficients obtained by Shiu et al. (1990) [16] using Equation 2.4 is presented in Table 2.5 below.

Table 2.5: Oil-water partition coefficients of six test oils reproduced from ref [16]

Component	Western Sweet Blend Crude	South Louisiana Crude	Prudhoe Bay crude	Gasoline	Fuel oil no. 6	Fuel oil no. 2
Pentane & Lighter	1883	1556	1043	2420	40	11
Benzene	121	106	75	228	72	80
Toluene	386	382	249	934	207	161
Ethylbenzene and xylenes	1105	1248	895	4758	568	524
Naphthalene	2126	1975	1947	5986	1178	2319
Methyl naphthalene	-	-	-	-	3930	5160
Dimethyl naphthalene	-	-	-	-	7716	42351

From the data presented in Table 2.5 above, the oil-water partition coefficient is highly dependent on the type/nature of the crude oil or petroleum product. The oil-water partition coefficient was highest with gasoline, while Fuel Oil no. 2 gave the lowest

partition coefficient for pentane, toluene, ethylbenzene and xylene. The variation of oil-water partition coefficient is as a result of changes in activity coefficients of the components depending on the nature of the matrix and hydrocarbon present [16]. This work has provided a solid basis for estimating the oil-water partitioning coefficient and how oil loading and crude oil type influences water solubility and partitioning coefficient of volatile and highly soluble compounds. However, it fails to detail how temperature and salinity will impact water solubility and partitioning in oil-water system.

2.4 Factors impacting partitioning of compounds in produced water

In general, an increase in temperature increases water solubility of PAHs and higher alkylated phenols [18]. Whitehouse (1984) [19]studied the effects of salinity and temperature on solubility of PAHs in water. In these studies, the temperature varied from 3.7 ^{0}C to 25 ^{0}C and salinity from 0 to 35 ppt. Solubility determination was by dynamic coupled column liquid chromatography (DCCLC). In this method, water is pumped through a column which has been coated with PAH under study. PAHs are then extracted from the saturated solution for analysis. Results obtained show that PAH solubility is not sensitive to small changes in salinity but is very sensitive to changes in temperature [19]. An increase in salinity tends to decrease water solubility of PAHs and phenols [19-22] with exception of 1,2-benzanthracene [19]. Although there are several studies [18, 19, 21] on the solubility of these compounds at varying temperature in pure water, there has been less study on the solubility and how these compounds partition in complex mixtures such

as produced water. The solubility of pure compounds in water can be predicted using the relation proposed by Schwarzenbach et al. (2003) [23]:

$$\ln C_{iw}^{sat}(L) = \frac{H_{iw}^{E}}{RT} + K . \qquad (2.5)$$

Where $C_{iw}^{sat}(L)$ is the concentration in the aqueous phase, H_{iw}^{E} is enthalpic contribution to the excess free energy, T is the temperature in Kelvin, R is the gas constant, i is analyte under study, K is constant, and w is water [23].

Equation 2.5 above can be used to predict solubility in water at varying temperature for some of the compounds under study and combined with Equation 2.6 to estimate the salting out effect.

$$C_{iw}^{sat}(salt) = C_{iw}^{sat} * 10^{-k_s[salt]} . \qquad (2.6)$$

$C_{iw}^{sat}(salt)$ is the corrected solubility at varying salinity, and k_{is} is the salting out constant, [salt] is the molar concentration of the salt in water.

Theoretical values were calculated using combination of equations (2.5) and (2.6). These solubilities were compared with experimental results obtained by Whitehouse (1984) and the results were presented in Figure 2.4 and 2.5.

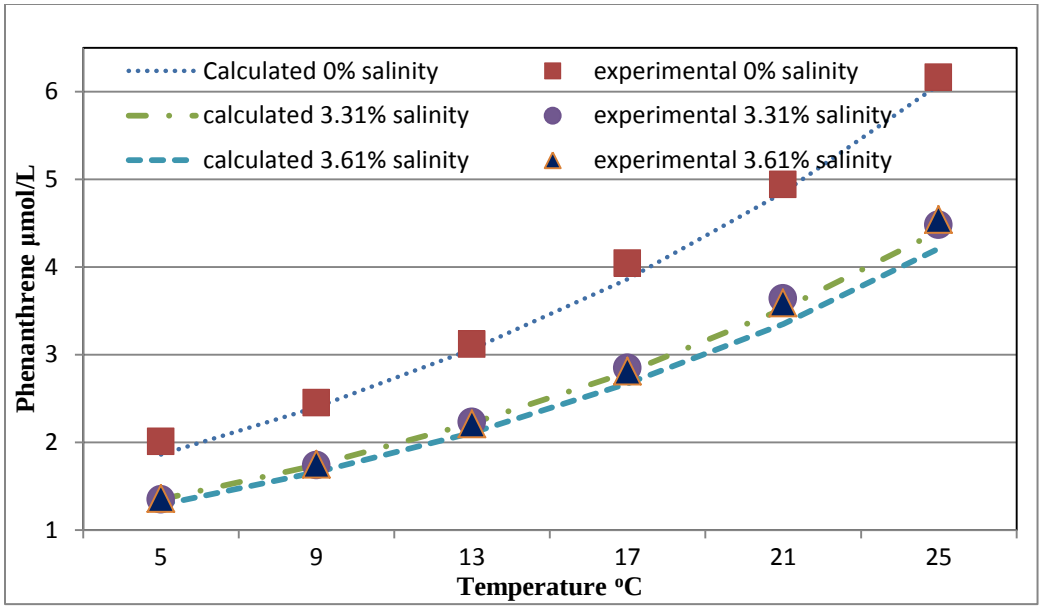

Figure 2.4: Calculated versus experimental [19] solubilities of phenanthrene as a function of temperature and salinity

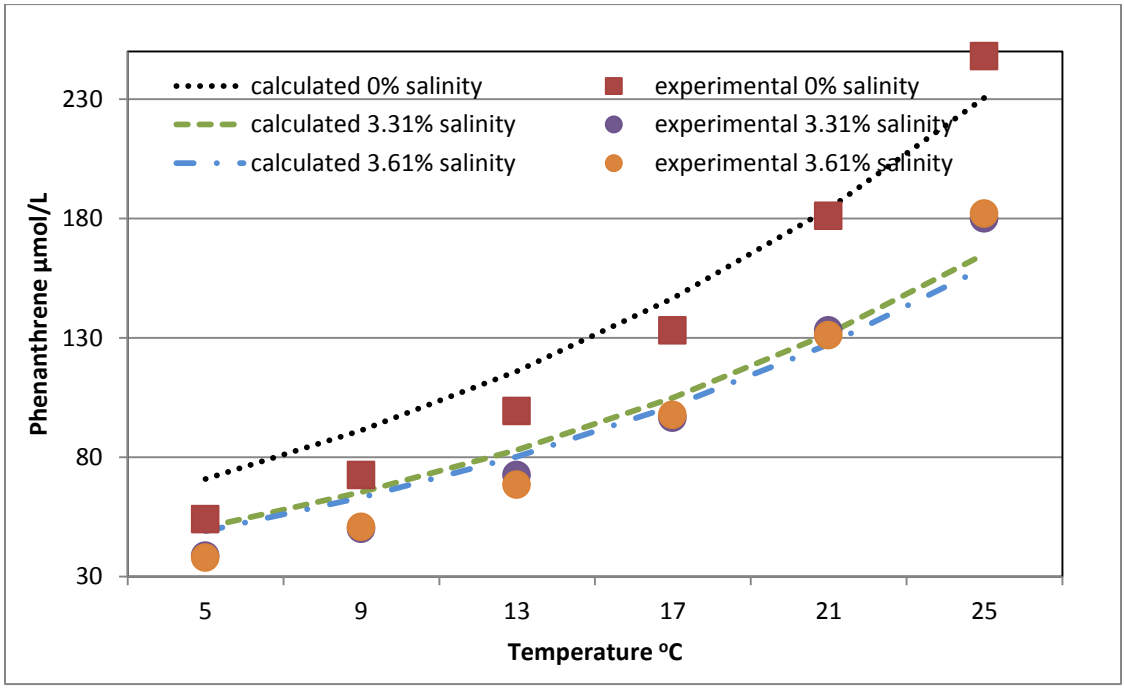

Figure 2.5: Calculated versus experimental [19] solubilities of anthracene as a function of temperature and salinity

From the Figures 2.4 and 2.5, it can be seen that anthracene and phenanthrene solubilities were impacted by temperature within salinity of 0 ppt and 36.5 ppt. At 0% salinity, solubilty of anthracene increased by 360% between temperature of 4.6^{o}C and 25.3^{o}C. While the solubility of phenanthrene increased by 200% within the same temperature range. The concentration of phenanthrene and anthracene also reduces with increasing salinity (salting out). The salting out effect gradually increases with increasing temperature.

There is a fairly good correlation between experimental and calculated solubility for phenanthrene at 0% salinity. However, significant discrepancies exist for anthracene between calculated and experimental result. This is not unexpected, since significant differences exist within published aqueous solubility data compiled by Yalkowsky et al. (2010) [18]. The results presented in Figures 2.4 and 2.5 clearly shows that salinity reduces solubility of PAHs while temperature enhances solubility. Therefore, there is a need to investigate these effects in a complex matrix such as produced water. Other factors that influences solubility and partitioning of compounds in produced water include: pH, dissolved total organic carbon [24], and added chemicals in the production line [2, 25].

Studies show that total organic carbon is one of the main factors influencing the fate, toxicity, and behavior of dissolved PAH in water column [24, 26, 27]. Organic carbon acts as a sorption platform for PAHs in the water column.

2.5 Produced water management

Produced water management can be grouped into four categories: technologies geared towards minimization of produced water production, reuse and recycling (reinjection), treatment, and disposal as the final option [4]. This section will focus on treatment options for produced water. A typical produced water treatment system is shown in Figure 2.6. The hydrocyclone is popular for the removal of oil and grease as well as sand and sludge, this is an important step in the many treatment processes. The degasser is usually used for the removal of poisonous gasses such as NO_X, SO_2, H_2S, etc. Additional treatment options to reduce the water soluble fraction include: membrane separation techniques, macro porous polymer extraction MPPE, and ion exchange, among others.

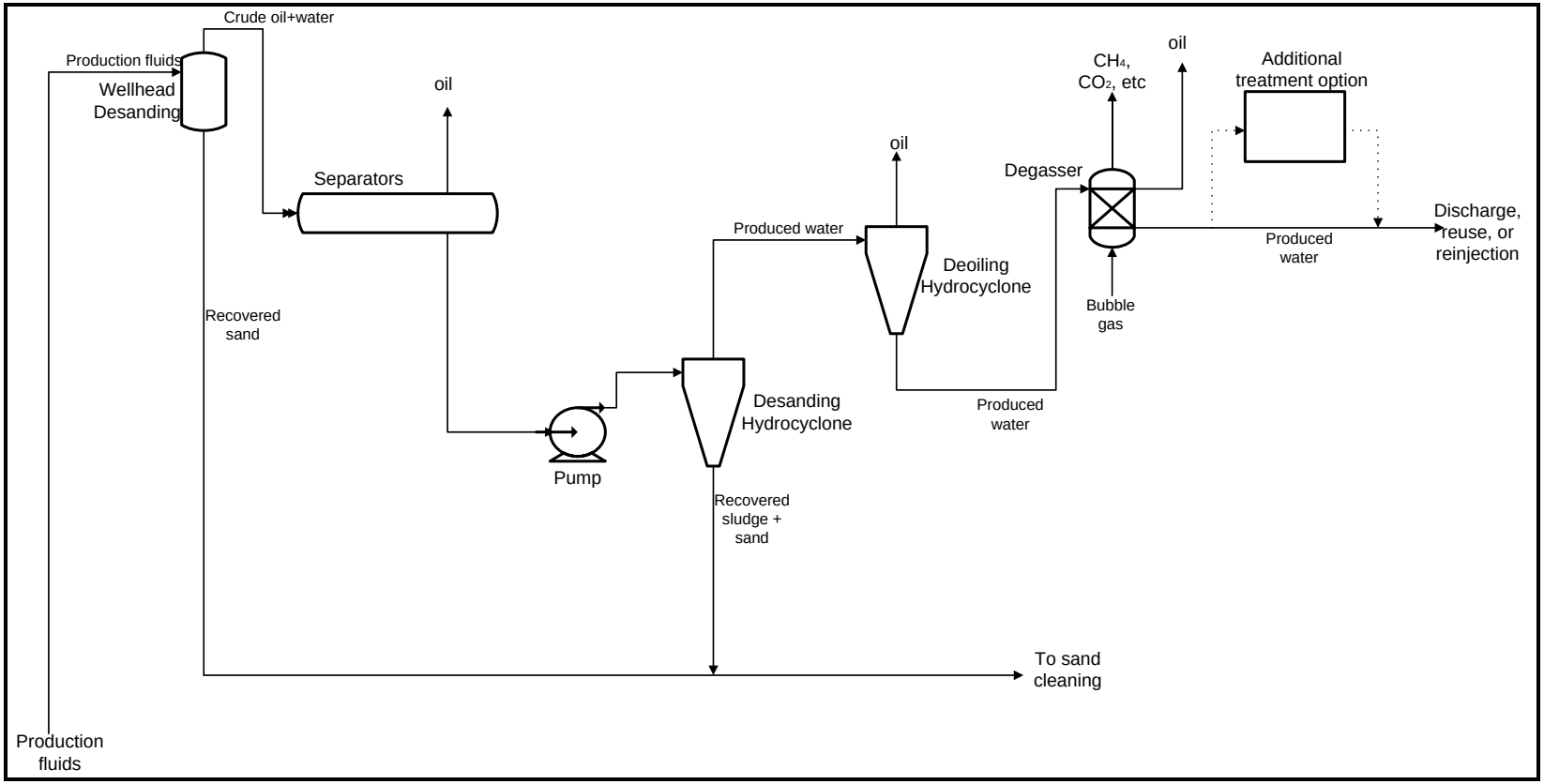

Figure 2.6: A typical produced water treatment train. Modified from reference [28]

Particular attention will be placed on treatment methods for produced water and how they impacts dispersed and dissolved fraction of contaminants included in the calculation of environmental impact factor. Produced water treatment techniques can be categorized into four; physical, chemical, biological, and membrane treatment [4].

Activated carbon and organoclay have been employed to remove both soluble and dispersed hydrocarbon in produced water. While activated carbon can absorb the soluble fraction it may be fouled by dispersed oils. Organoclay can remove the dispersed oil in produced water. The major challenge with this method is that suspended particles tend to block the pores of the activated carbon and thereby reduce their removal efficiency. Other problems with this technique include capacity issues and secondary waste generated from regeneration of absorbers [4]. Cyclones are very popular for the removal of dispersed oil in produced water but lack the capability to remove the dissolved fraction. Dissolved air precipitation has been employed for the removal of dissolved ethyl benzene, octane, and micro dispersed decane with efficiency of 40%, 95% and 75% respectively [4]. C-Tour is a produced water treatment system that aims to reduce the dispersed oil in water. Field trials shows removal efficiency of 70%, 60%, and 20% for 2-3 ring PAHs and NPD (naphthalene, phenanthrene, dibenzothiophene), C6 phenols, and C4-C5 phenols respectively [8]. Studies show that C4+ alkyl phenol is the most important contributor to environmental impact from produced water followed by aliphatic hydrocarbons and PAHs [9, 13]. The implication of the phase behavior of these contaminants is that produced water treatment system that reduces the concentration of dispersed oil will reduce the environmental impact of PAHs and C4+ alkylated phenols [8, 12].

Chemical precipitation of suspended solids (SS) and dispersed oil in produced water can be reduced >92% and 97% respectively through coagulation and flocculation. These methods however is not suitable for dissolved fractions [4] and further clean up requires significant space, a challenge in the Arctic and offshore.

Membrane separation usually incorporates one or a combination of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). MF, UF, NF, and RO can be used to separate suspended particles, dispersed oil, small fines of oil droplets in the water column, and dissolved and ionic components respectively. UF have been shown to reduce BTEX by 54% [4]. Meijer et al (2001) demonstrated the use of Macro Porous Polymer-Extraction Technology for produced water treatment. BTEX can be reduced from influent concentration of 150 mg/L to 6 mg/L, whereas dispersed oil was removed by only 50 wt% because the MPPE was designed to remove aromatics in produced water. Therefore it will be preferable to use MPPE in combination with hydrocyclone and other systems that reduce dispersed oil. Field and commercial test of MPPE show >99% removal of PAHs but only 30% removal efficiency was obtained with alkyl phenols [8, 29]. MPPE has not been tested in more remote and arctic regions. In harsh/cold regions otherwise soluble contaminants in produced water could partition to the dispersed oil which will facilitate their removal by conventional treatment methods [7]. BTEX volatility decreases with temperature and will likely remain in the aqueous phase in cold regions.

2.6 Fate of discharged produced water

Produced water discharged into the marine environment undergoes dispersion and dilution, evaporation, sedimentation in marine environment, biodegradation, chemical oxidation, bio-concentration in plankton, bioaccumulation and biomagnification [3]. Dilution can be conceived to be in two stages: turbulent dilution within minutes of discharge and laminar dilution several hours after discharge [30]. The dilution rate can be as high as 1000- fold within 100 meters of discharge [31]. For NPD, dilution rate of up to 150,000 is achievable within 50 meters of the discharge location [31]. Meanwhile, dilution rate was found to be between 1,000 and 5,000 for PAHs, mainly because PAHs have higher molecular weights compared to BTEX and NPD compounds [31].

The rate of biodegradation of BTEX and NPD is high in the water column after discharge [32]. PAHs are partially soluble and can be degraded by photo-oxidation and biodegradation [32]. While photo-oxidation of PAH occurs mainly at the water surface, biodegradation occurs in the water column. OGP (2002) monitored the concentration of naphthalene and PAHs in water column at various distances from a discharge location in the Norwegian sector of the North Sea. Results obtained shows that concentration of naphthalenes and PAHs rapidly diminishes at 500 m from discharge location as presented in Table 2.6

Table 2.6: Fate of naphthalenes and PAHs at different locations from discharge point

	Concentration in (μg/L) of naphthalene and PAHs			
	in PW	at 500 m	at 2000 m	at 10000 m
Naphthalenes	1200	0.040	0.013	0.007
PAHs	33	0.004	0.001	0.0004

Frost et al. (1998) , as cited in Ekins et al. (2005) [3], detected PAHs concentration above seawater concentration at a distance of 10 km from point of discharge. Models that incorporate dilution, dispersion, and biological degradation predict higher concentrations even at farther distances from release location [3]. Brendehaug et al. [33] assert that more than 95% of dissolved organic carbons are degraded within 28 days, with 80 - 90% degraded within the first week. More than 99.9% of the phenol in the samples was not detectable within one week. The biodegradation of alkylated phenols reduces as the number of carbon atoms bonded to the aromatic structure increases [33]. However, elevated levels of short chained alkylphenols and NPD compounds were found within 2 km of the discharge location from a Norwegian oil platform [34]. Higher alkylated phenols have been found to persist in water several days after discharge [33]. Table 2.7 summarizes degradation of phenols within the first twenty eight days of discharge.

During storage, biodegradation did not play a significant role [35]. Samples stored for four days under dark at $4^{o}C$ show no change in concentration of compounds of environmental concern in produced water [35]. It was discovered that, temperature did not influence biodegradation of phenols, PAHs, TPH, and BTEX over a four day period

when stored at 28 ^{o}C [35]. However, the produced water samples diluted with filtered sea water were degraded over the four day period. It is therefore likely that, the produced water sample from platforms where sea water reinjection is employed is likely to be susceptible to biodegradation compared to fields where there is no water injection.

Table 2.7: Biodegradation of samples [33]

Compound	**Initial**	**Day 7**	**Day 21**	**Day 29**
EOM (mg/L)	25.6	7.18	4.52	1.526
Phenol (μg/L)	5120	3.84	1.65	1.08
C1-phenol (cresol) (μg/L)	2450	1.78	0.270	0.330
C2-phenol (μg/L)	396	11.1	1.90	1.50
C3-phenol (μg/L)	130	36.4	7.88	6.19
C4-phenol (μg/L)	26.2	16.6	21.0	3.39
C5-phenol (μg/L)	16.8	12.2	4.60	2.96
C6-phenol (μg/L)	13.3	12.2	9.64	4.41
C7-phenol (μg/L)	5.49	4.61	4.36	3.34
Total phenol (μg/L)	8160	91.0	51.3	23.2

Most of the studies on fate of produced water were carried out in the North Sea. In more remote, cold, and harsh climate like offshore Newfoundland and Labrador, the fate of discharge produced water could be complex; ice encapsulation, high motion, cold temperatures, seasonal variation in UV photo-oxidation and biodegradation make the fate different from open oceans. The presence of UV light will increase the biodegradation of oil and surface toxicity [36].

The major organic contaminants in produced water are: BTEX (benzene, toluene, ethylbenzene and xylene); phenols and alkylphenols; PAHs (polycyclic aromatic hydrocarbons). PAHs and C6+ alkylphenols exist mainly in the dispersed oil phase, while others such as BTEX and C0-C3 alkylated phenols are soluble in water. Water solubility of the components within the group of naphthalenes and C4-C5 phenols varies depending on the degree of alkylation. However, if the dispersed oil content is reduced to 40 mg/L, the contaminants of concern will shift towards the PAHs and BTEX. This clearly demonstrates that the reduction of dispersed oil in water does not reduce the dissolved fraction of produced water. Temperature, salinity, and dissolved organic carbon influence the solubility of aromatics and phenols in produced water. Increasing temperature generally enhance solubility of aromatics in pure water, while increase in salinity tend to reduce solubility of aromatics and phenols in produced water. The effect of temperature and salinity on partition behavior of aromatics and phenols in complex system such as produced water is less studied. Faksness et al. (2004) [12] is the only known work in literature that attempts to determine how the contaminants of environmental concern in produced water partition between the dispersed oil phase and dissolved aqueous phase. However, temperature was not varied or specifically indicated in this study. The rest of this thesis explored the effect of temperature and salinity on solubility and partitioning of contaminants in produced water.

Chapter 3: Methods and procedures

3.1 Materials

All solvents used were of America Chemical Society (ACS) reagent grade. Dichloromethane, methanol, hexane and acetonitrile (Hypersolv) were obtained from Fisher Scientific (Canada), and sea salt from Sigma Aldrich (Canada). All standards were of gas chromatography GC analytical reagent grade purchased from Sigma Aldrich (Steinheim, Germany). The following analytical standards were used: acenaphthene-d10, naphthalene, pyrene, chrysene, dibenzothiophene, phenol, p-cresol, 4-tert-butylphenol, and fluorene. All were of high quality standard with purity of 99.9% and matches National Institute of Standards and Technology (NIST) mass spectral library. Produced water sampling bottles were made of amber glass with Teflon (lined) screw caps. The bottles were procured from Fisher Scientific (Canada) and have been pre-cleaned to meet or exceed EPA standard for environmental water sampling bottles. Two-liter bottles were used for offshore sampling, while subsamples were collected using 125 mL amber bottles. Micro Kuderna-Danish concentrator was obtained from SUPELCO (PA, USA). Produced water samples were supplied by a Newfoundland and Labrador oilfield operator.

3.2 Produced water sample collection and handling

Measurement of compounds in offshore produced water start with obtaining samples that is typical of the matrix being sampled and ensuring that sample integrity is not

compromised prior to analysis. Amber borosilicate glass bottles with PTFE-lined screw caps are normally recommended for sampling and generally handling produced water. This is because: plastics may leach plasticizers to the sample and lead to interference with subsequent chromatographic analysis; potential loss of compounds during transit and storage as some plastics are known to be porous to certain volatile compounds; biodegradation of certain compounds at the surface of plastics due to possible microbial encampment [37].

Produced water sample collection follows the "Guidance notes for The Sampling and Analysis of Produced Water and Other Hydrocarbon Discharges" [38] prepared by the UK department of energy and climate change. Samples were collected after the medium pressure MP separator (i.e. after separation of the water from crude oil) before any treatment using pre-clean two liters amber glass bottles with Teflon lined screw caps. The 2-L bottles were filled leaving no air gap with a representative sample from the sampling point. The bottle was then secured with the Teflon lined caps and inverted six times to check for leaks. Sample filled bottles were packed inside opaque coolers (to prevent ingress of UV light) and cooled with ice paks. The samples were then transported to onshore laboratory for processing where it was received in the laboratory within eight hours of sample collection. Upon receipt, samples were cooled to below 4^{o}C to suppress activity of thermophilic bacteria that may degrade certain compounds of interest. The salinity of produced water was tested using portable Orion star conductivity meter and pH was measured using desktop Metler pH meter.

3.3 Experiment Set up

The settling experiments were carried out in the laboratory. Samples were transferred from the amber glass bottles into aspirators bottles (filled to 90% volume as shown in Figure 3.1) with a drain tap at the bottom and an inert stop cock. The samples were shaken together at the start of experiment to obtain a uniform mixture. The set up was then place in an Innova incubator 4230 at a set temperature and duplicate subsamples were collected at 0 hrs, 12 hrs, 24 hrs and 48 hrs. These subsamples were immediately adjusted to pH of <2 using hydrochloric acid 50% solution. Temperature and salinity were considered as factors that influences partitioning of the target contaminants in produced water. Temperature was varied at six levels: 4^{o}C, 9.5 ^{o}C, 15 ^{o}C, 26 ^{o}C, 50 ^{o}C, and 70 ^{o}C. Two salinities levels of 46.8 part per thousand (ppt) and 66.8 ppt were tested. Sample was received at 46.8 ppt in the laboratory and sea salt was used to adjust salinity to 66.8 ppt for another set of experiment. Forty grams of sea salt was dissolved in two liters produced water sample to raise the salinity to 66.8 ppt. The factors and levels considered were summarized in Table 3.1. This involves 14 experimental runs.

Table 3.1: Test Samples

Run	Temp (^{o}C)	Salinity (ppt)
1	4.0	46.8
2	9.5	46.8
3	15	46.8
4	26	46.8
5	4.0	46.8
6	15	46.8
7	26	46.8
8	50	46.8
9	70	46.8
10	4.0	66.8
11	9.5	66.8
12	15	66.8
13	26	66.8
14	50	66.8

The test samples is as shown in Figure 3.1 below. Subsamples were collected in 125 mL amber glass bottles with Teflon lined screw caps. Subsamples were collected in duplicate.

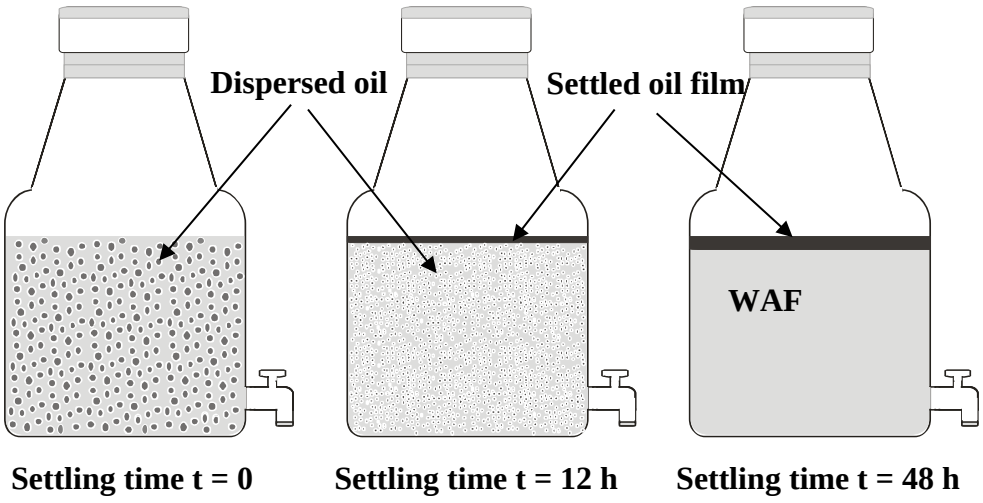

Figure 3.1: Experiment set up [12].

3.4 Sample preparation

3.4.1 Sample Extraction

Sample preparation was performed as outlined in EPA610. The samples for PAHs/Phenols were serially extracted using manual liquid-liquid extraction with dichloromethane (DCM) as the extraction solvent. Each sample was spiked with acenaphthene-d10 as surrogate internal standard and serially extracted three times using 10 mL of DCM each time. A 125 mL portion of produced water sample was transferred to a 250 mL separating funnel, 10 mL of dichloromethane was added to the flask and the content was shaken together for three minutes with periodic venting (this releases pressure build up in the flask). The set up was clamped onto a retort stand and allowed to settle for 10 minutes. The DCM layer was collected into beaker by carefully opening the drain valve. The extraction was repeated two more times to get quantitative recovery of all analytes. All the three extractions were collected into same collection vessel. Sample clean-up was not necessary as there is no interference in the GC-MS chromatogram obtained. 200 ppm of standard solution was prepared by accurately weighing 20 mg of each of the analytical standards and dissolving it in 100 mL of DCM in a volumetric flask.

3.4.2 Sample Concentration

Sample concentration was carried out using the micro Kuderna-Danish (K-D) concentrator. The micro K-D concentrator was assembled by attaching a 2mL

concentrator tube to a 50 mL evaporative flask. The combined extract was poured through a solvent rinsed granular sodium sulfate, which is held in a funnel with a high-quality grade filter paper and the extract was collected in the micro K-D concentrator. The flask was rinsed with 5 mL DCM to complete the quantitative transfer. The Snyder column was pre-wet by adding about 1 mL of DCM to the top of the column. The micro K-D apparatus was placed on a hot water bath (45-55°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor [39]. The vertical position of the apparatus and the water temperature was adjusted as necessary to complete the concentration in 30-45 minutes. When the apparent volume of liquid reaches 2 mL, the micro K-D apparatus was removed and allowed to drain and cool for at least 10 minutes. The Snyder column was removed, the flask and its lower joint was rinsed into the concentrator tube with 1 mL of DCM. Sample analysis with GC-MS was usually carried out immediately. Whenever samples have to be kept overnight, they are transferred to 8 mL amber vials with Teflon screw caps and stored at -25^{o}C in the freezer. To quantify PAHs/phenols the method of standard addition was employed.

3.5 Chemical Analysis

Quantification of phenols and PAHs was carried out by a method of standard addition. The final concentrated solution was divided to four equal aliquots. And three of the four aliquot were spiked with 10 μL, 30 μL and 50 μL standard solutions of target analytes. Each of the four aliquot was made up to 1 mL each with DCM.

Concentrations of each compounds were determined from analysis using GC-MS operating in the selective ion monitoring (SIM) mode. This optimizes sensitivity and enables specificity. To quantify dispersed oil, the extracts were also analyzed for total extractable organic compounds (TEOCs). Sample extract from the PAHs and phenol were also analyzed using GC-MS method specified in Table 3.4 [40]. Quantification of the dispersed oil was done by external calibration curve based on the crude oil from the same platform [12]. Calibration covers hydrocarbons in the range C10-C40 aliphatic hydrocarbon.

3.5.1 Gas Chromatography

The following summarizes the gas chromatography mass spectrometry conditions used, its parameter and analyte quantification. All analyses were performed on an Agilent Technologies 6890N gas chromatograph fitted with an Agilent 5973 mass spectrometer. Chromatographic resolution is achieved with a 30 m × 0.25 mm DB-5ms capillary column which has a 0.25 μm film thickness with helium carrier gas. The phenols and

PAHs analyzed in this study are listed in Table 3.2 along with the retention times and their mass spectra

Table 3.2: Gas Chromatography conditions

Analyte	Retention time (min)	Mass spectrum (m/z)
Phenol	4.2	39, 66, 94
P-cresol	4.9	107, 77, 79, 90, 108
Naphthalene	6.2	127, 128, 129
4-t-butylphenol	7.6	135, 107, 135, 136, 150
Acenaphthene d10	10.2	160, 162, 163, 164
Fluorene	11.4	165, 166, 167, 168
Dibenzothiophene	13.1	139, 184, 185
Phenanthrene	13.4	89, 176, 178, 179
Pyrene	16.2	101, 200, 202, 203
Chrysene	18.5	226, 227, 228, 229

3.5.1.1 Instrument Parameters

Gas chromatographic parameters are presented in table 3.3. The GC oven temperature program for phenols/PAHs and TEOCs are given in Table 3.4 and 3.5 respectively.

Table 3.3: Chromatography parameters

Carrier gas:	Helium (99.999%)
Injector:	On Column, Constant Flow
Injection volume:	1 μL
Mode:	Splitless
Transfer line:	300EC

The mass spectrometer is operated in the electron ionization (EI) mode with ion source and quadrapole temperatures of 230^{o}C and 100^{o}C respectively.

Table 3.4: GC oven temperature program for phenols/PAHs analysis.

Initial temperature: 40 ^{o}C (on) Equilibration time 0.5 min Initial time: 1 min		
Rate (^{o}C/min)	Final temperature (^{o}C)	Final hold time (min)
30	130	3.00
14	180	0.00
12	240	0.00
14	300	1.00
Total run time: 20.86 min		

Table 3.5: GC oven temperature program for dispersed oil analysis.

Initial temperature: 40^{o}C Initial time: 2 min		
Rate (^{o}C/min)	Final temperature (^{o}C)	Final hold time (min)
15	280	4
10	300	5
Total run time: 29.0 minutes		

3.5.2 Standard Addition

In a complex matrix such as PW, the intensity of the signal of the analyte is affected by the composition of the matrix. To overcome this problem, the method of standard addition is usually employed. However, before method of standard addition can be applied, two conditions must be satisfied:

(a) The calibration curve must be linear,

(b) The calibration curve of the analyte nearly almost passes through the origin.

In this technique, standard solutions with known concentrations are added to one or more aliquots of the processed sample. This will compensate for interruption of the analyte signal by the matrix.

In this discourse, portions of the standard solution 10 μL, 30 μL, and 50 μL were added to three (of the four) aliquots of the concentrated sample. Each aliquot is made up to 1 mL with DCM. This ensures the matrix was not affected by the addition of standard solution. And the samples analyzed by GC-MS, the concentration of added standard solution was calculated in each sample and plotted against signal response area (area under the chromatogram peak of each analyte). Figure 3.2 below shows a typical plot of signal response area vs concentration of standard solution in sample.

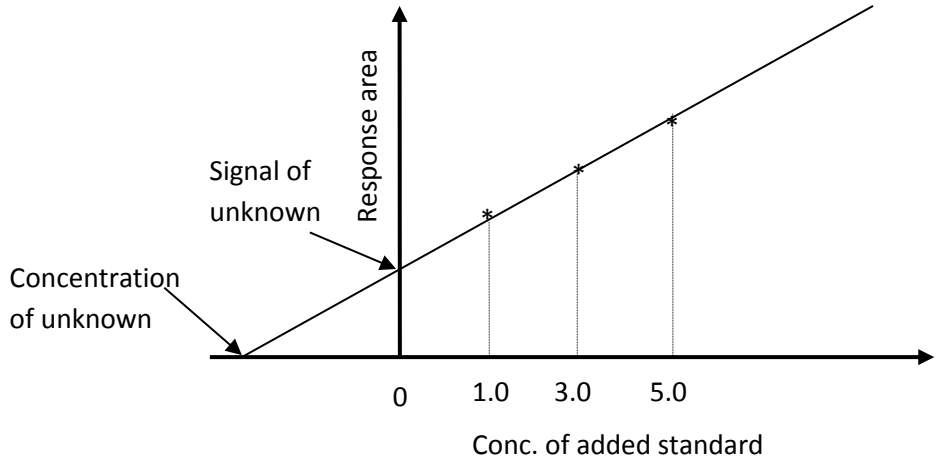

Figure 3.2: Typical plot for determination of analyte concentration by standard addition

To determine the concentration of the analyte, the line is extrapolated to the concentration axis. This point, where the signal (response area) is nearly zero, represents the

concentration of the analyte. Figure 3.3 shows the calibration curve for p-cresol and phenol at salinity of 46.8 ppt and 0^{o}C.

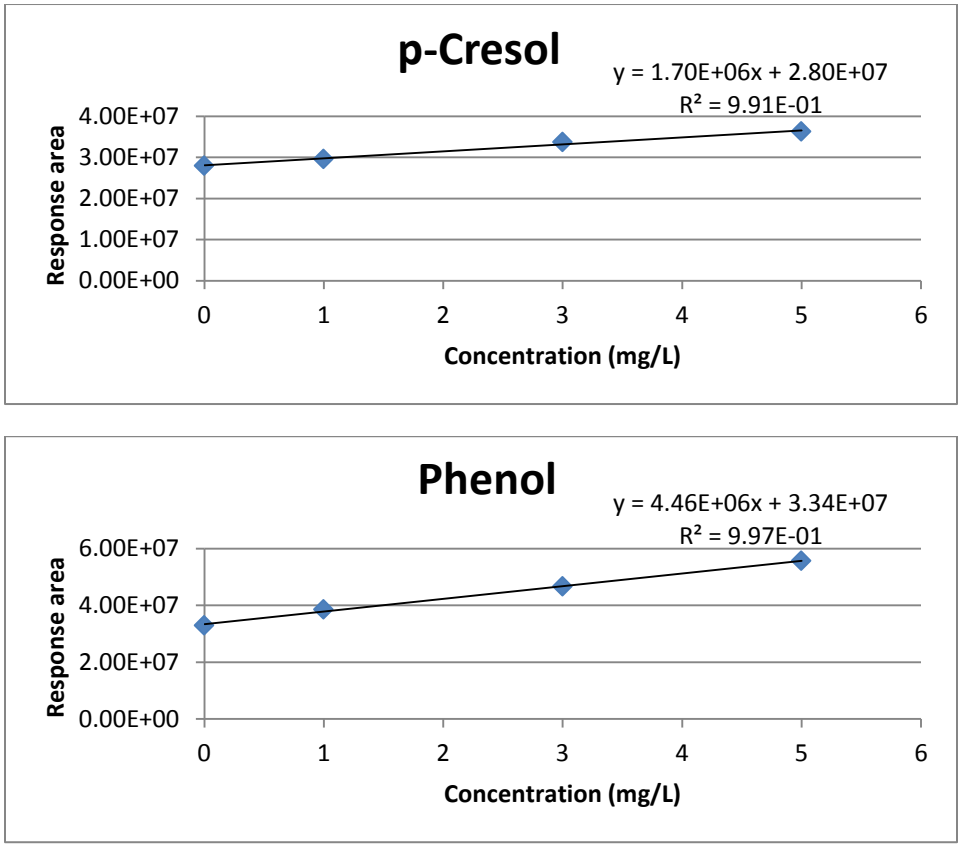

Figure 3.3: Calibration curve for p-cresol and phenol at salinity of 46.8 ppt and 0^{o}C.

3.6 Steady state modeling of produced water treatment system

In recent years produced water discharge criteria has become more stringent and regulators are demanding for reduction in compounds of environmental impact in addition to oil in water discharge criteria. As the oil field becomes mature and produced water volume increases, it becomes increasingly challenging for the existing treatment

system to adequately reduce the oil in water within discharge criteria. In remote offshore location, introduction of additional treatment equipment to improve on the existing system is difficult due to limited space and adverse environmental conditions. To improve on existing treatment system there is need to understand the parameters that influence efficiency and phase and partitioning pattern on compounds in produced water as they pass through the treatment system. Aspen HYSYS is a comprehensive modeling tool that enables accurate calculation of physical properties, transport properties, and phase behavior for the chemical, oil & gas, and refining industries. Aspen HYSYS V8.6 will be used to model produced water treatment system with emphasis on the phase behavior and partitioning pattern of selected compounds in produced water. The efficiency of the system will be investigated and factors that affect performance of process equipment explained.

3.6.1 Process flow Diagram

The produced water treatment model was developed based on industry data. The model configuration consist of a mixer that combines crude oil and water, a pump to provide a means of increasing the pressure head of the feed stream, a cooler to enable variation of inlet temperature of feed into the hydrocyclone, a hydrocyclone for separation of oil from water, and a three phase separator used in the absence of degasser in Aspen HYSYS for venting off gasses. The model diagram as developed in HYSYS is shown in Figure 3.4.

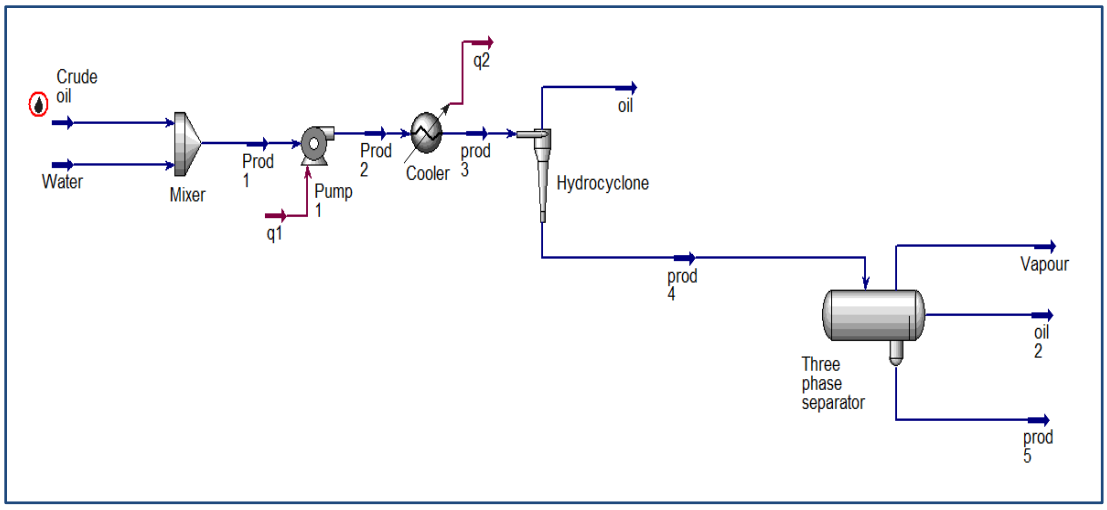

Figure 3.4: Produced water process flow diagram in Aspen HYSYS V8.6

The feed comprises of crude oil and water mixed together. The water was spiked with phenol, p-cresol, naphthalene, fluorene, phenanthrene and pyrene. Table 3.6 shows the concentration of the analytes in the water which represent average concentrations obtained from experiment conducted on produced water obtained from oil producing platform from offshore Newfoundland. The produced water samples was collected after the medium pressure separator before the hydrocyclone.

Table 3.6: Concentration of components in water

Analytes	Concentration µg/L
Phenol	1010
p-Cresol	710
Naphthalene	200
Fluorene	15
Phenanthrene	150
Pyrene	10

The petroleum fluid was characterized by using crude assay from offshore Newfoundland and Labrador. SRK-Twu fluid package was used to model thermodynamic and transport properties since the popular Peng-Robinson fluid package was not suitable for p-cresol and pyrene. Details of the assay development and flow conditions will be discussed in detail in chapter 5. The crude oil and water were mixed together in the mixer as shown in figure 3.3. The mixer was designed to set outlet pressure to the lowest inlet stream pressure. The pump operates adiabatically at 75% efficiency, the cooler provide a means of varying the feed temperature into the hydrocyclone. In the design of the hydrocyclone, the assumptions made are shown in Figures 3.5 and 3.6.

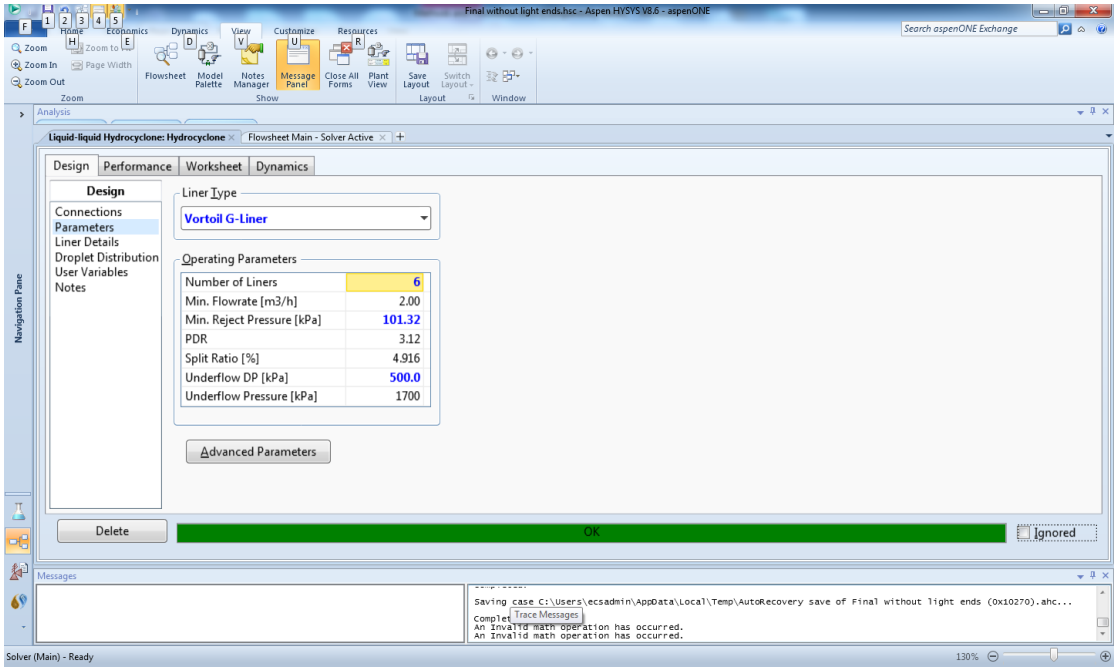

Figure 3.5: Design parameters of hydrocyclone

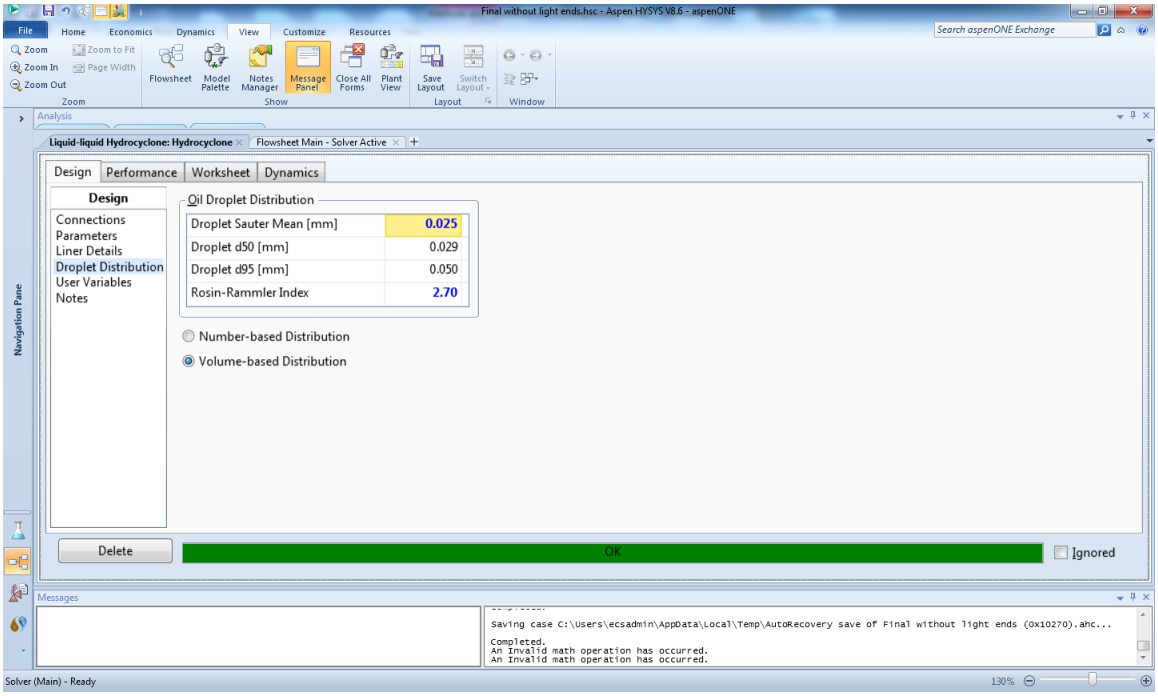

Figure 3.6: Oil droplet distribution used in the design of hydrocyclone

The three phase separator was used in place of degasser in the produced water treatment train. HYSYS does not have degasser in model palette.

SRK-Twu fluid package was used. The popular Peng-Robinson fluid package was not suitable for p-cresol and pyrene. The crude oil assay TBP curve is shown in Figure 5.1.

Chapter 4: Results and Discussion

All the samples were analyzed for total extractable organic compounds (TEOCs) otherwise known as dispersed oil. Table 4.1 and 4.2 shows the average dispersed oil concentration of WAF as a function of time. The concentration of dispersed oil in the water phase drops rapidly between settling time zero and 12 h across all temperatures and salinity tested. It was observed that samples from experiments at 66.8‰ salinity were more turbid than samples from experiments at 46.8‰ salinity. However, the measured concentration of dispersed oil is not statistically different between the two salinity levels. Two sample t test conducted returns a p value >0.4. A p-value greater than 0.05 indicates there is no statistical difference between the two experiments conducted at 46.8‰ and 66.8‰ salinities.

Table 4.1: Dispersed oil concentration (mg/L) at 46.8‰ salinity

Temperature ^{o}C	Time (h)			
	0	**12**	**24**	**48**
4	134	18	14	8
9.5	108	18	10	5
15	126	10	5	3
26	121	19	7	5
50	148	8	8	3
70	88	7	6	2

Table 4.2: Dispersed oil concentration (mg/L) at 66.8‰ salinity

Temperature ^{o}C	Time (h)			
	0	**12**	**24**	**48**
4	145	18	15	9
9.5	80	18	8	5
15	175	10	6	5
26	120	17	8	6
50	140	12	7	6

The dispersed oil concentration in the water phase drops from 134 mg/L at the start of the experiment to 8 mg/L after 48 h for experiment conducted at 4 ^{o}C and 46.8‰ salinity. The dispersed oil rises to the surface as the experiment progresses and equilibrium has been established at 48 h as there is no change in dispersed oil concentration between 24 h and 48 h. In the following section, details of how the target contaminants in produced water partition between the water phase and oil phase will be discussed. The effect of temperature and salinity on the partitioning trends for these compounds will be highlighted. In the course of the experiment, it was discovered that the concentration of target analytes varied slightly from one sampling bottle to another. This is as a result of differences in the process conditions in the separation train over the period of sample collection. Since it was not feasible to obtain a uniform sample across all experiments conducted, results obtained were normalized to provide a basis for analyzing the effect of temperature. By normalization, the original data were mapped into a scale of one. That is the data were divided by the highest value in the group. This may introduce bias if the

highest value is not within the error band presented. Both original and normalized data are presented.

4.1 Effect of temperature and salinity on partitioning behavior of Phenol

The results obtained from the settling experiment are presented in Figure 4.1 and 4.2.

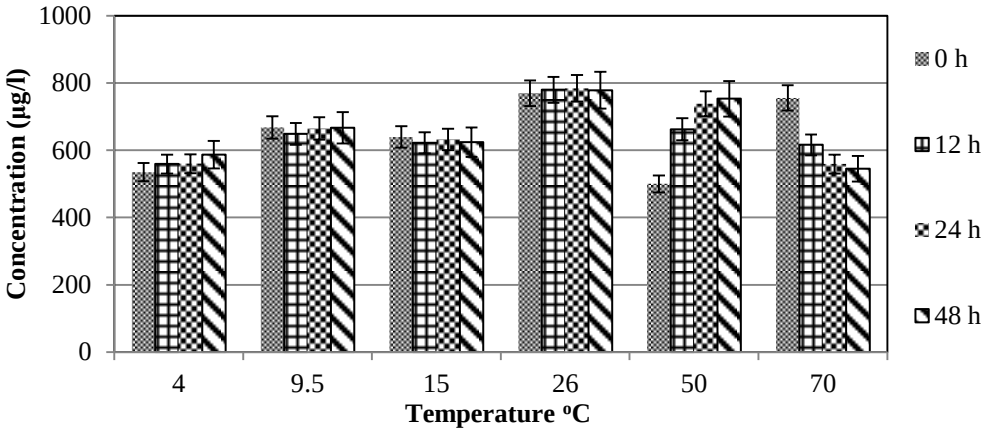

Figure 4.1: Results from settling experiment for phenol at salinity of 46.8‰ and settling time of 0 h to 48 h.

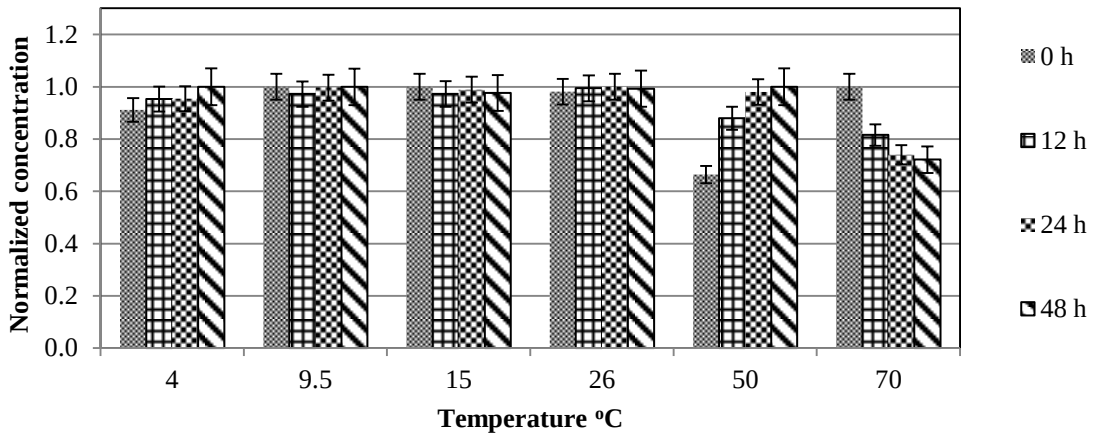

Figure 4.2: Normalized results from settling experiment for phenol at salinity f 46.8‰ and settling time of 0 h to 48 h.

The concentration of phenol remains constant from the start to the end of experiment as dispersed oil concentration drops from 134 mg/L to 8 mg/L for experiment conducted at 4 ^{o}C. Similarly, there is no change in phenol concentration for experiments conducted at 9.5 ^{o}C, 15 ^{o}C, and 26 ^{o}C. While there is an apparent increase in phenol concentration at 50 ^{o}C, the phenol concentration drops at temperature of 70 ^{o}C. This could be as a result of increase in vapor pressure with increasing temperature, and/or biodegradation as result of increased activities of thermophilic bacteria found in produced water at higher temperature. Thermophilic bacteria have been found to be ubiquitous in oil field produced water [35, 41]. Thermophilic bacteria have been shown to be most active at temperatures between 50 ^{o}C and 80 ^{o}C. These bacteria form spores at temperatures above 110 ^{o}C and exhibit no growth rate below 37 ^{o}C [42, 43].

From the foregoing, reduction of dispersed oil concentration will not reduce the concentration of phenol in the water phase. Phenol concentration in the water phase does not correlate to the dispersed oil concentration. This is in agreement with published data [12]. Therefore produced water treatment options that reduce oil and grease, such as deoiling hydrocyclone, will not reduce the concentration of phenol in the produced water. Furthermore, solubility of phenol in produced water is not significantly influenced by temperature within 4 ^{o}C and 26 ^{o}C. Therefore it can be concluded that the partitioning behavior of phenol is not influenced by the dispersed oil concentration in the water phase and temperature does not influence the concentration of phenol within the temperature range of 4 ^{o}C and 26 ^{o}C. Within experimental error, there is no change in concentration of

phenol at temperatures of 4 ^{o}C, 9.5 ^{o}C, 15 ^{o}C, and 26 ^{o}C as the dispersed oil settles to the surface from time zero to forty eight hours. This was also observed by Faksness et al. (2004) [12]. At 50 ^{o}C there is an increase in phenol concentration in the WAF. So at 50 ^{o}C more phenol is likely to go into the water phase. It can be inferred that the contribution from micro oil droplet (Equation 2.3) to the aqueous concentration of phenol is negligible. For the experiment conducted at 66.8‰ salinity, similar effect was observed. The concentration of phenol remains unchanged for experiments conducted at 4 ^{o}C, 9.5 ^{o}C, 15 ^{o}C and 26 ^{o}C within experimental error as shown in Figure 4.2.

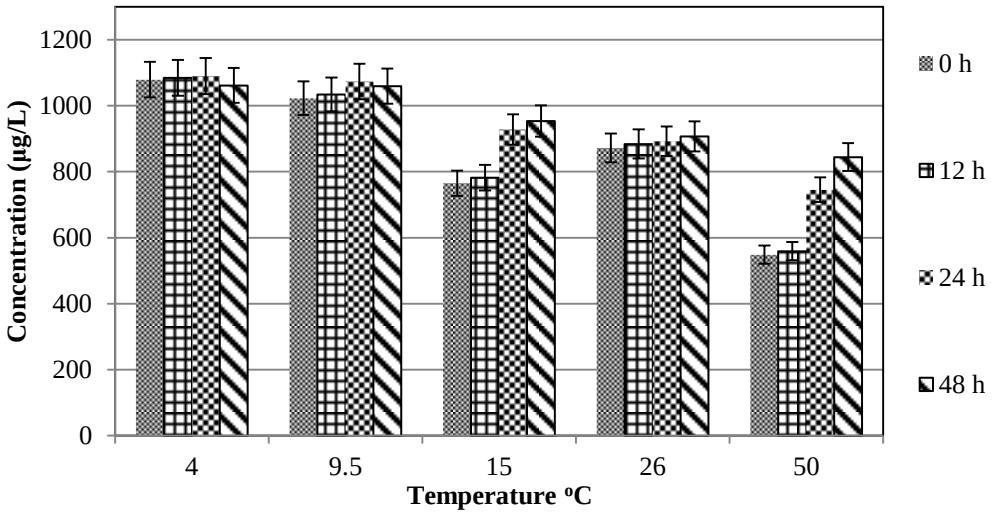

Figure 4.3: Results from settling experiment for phenol at 66.8‰ salinity and settling time of 0 h to 48 h.

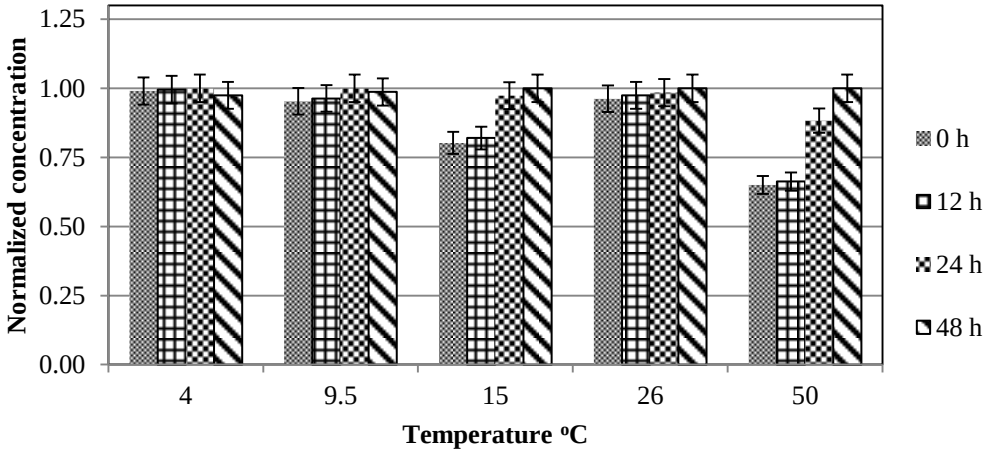

Figure 4.4: Normalized results from settling experiment for phenol at 66.8‰ salinity and settling time of 0 h to 48 h.

The trend at 66.8‰ salinity is closely related to that of 46.8‰ salinity. However, the observed concentration at 66.8‰ is higher than concentration recorded at 46.8‰ salinity. Increase in salinity enhances liquid-liquid extraction and recovery of phenol. This effect was reported in 2005 by Correia et al. [44].

4.2 Effect of temperature and salinity on partitioning behavior of p-cresol and 4-tert-Butylphenol

The partitioning behavior exhibited by p-cresol and 4-tert-butylphenol were closes related to partitioning behavior of phenol. The concentrations of p-cresol and 4-tert-butylphenol in the water phase are shown in Figures 4.3 and 4.4.

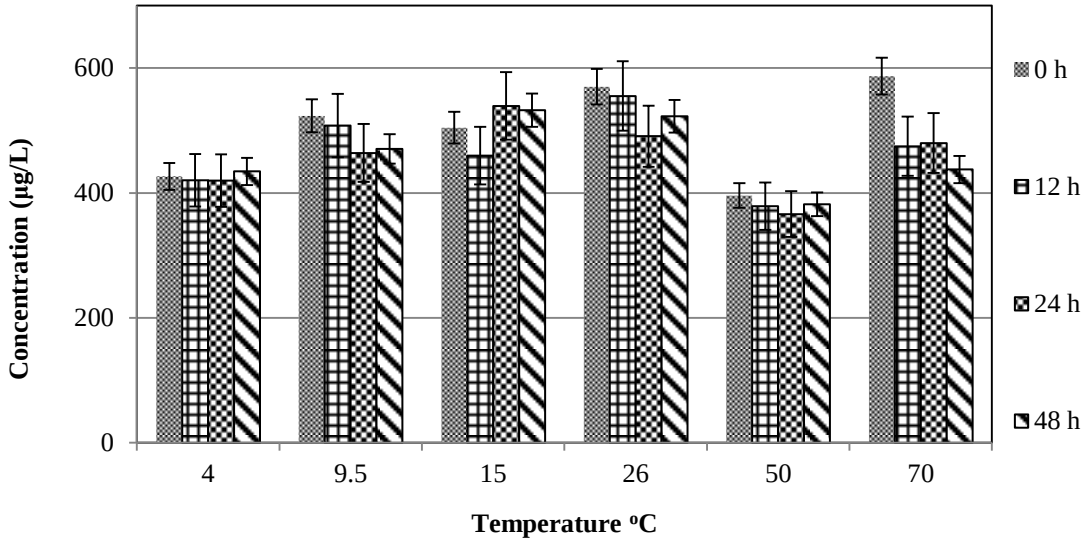

Figure 4.5 Results from settling experiment for p-cresol at salinity of 46.8‰ and settling time of 0 h to 48 h

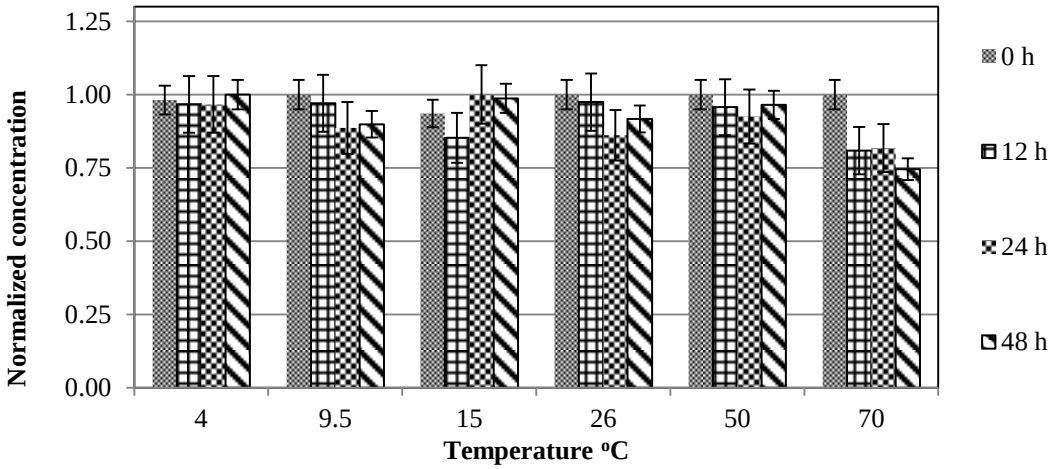

Figure 4.6: Normalized results from settling experiment for p-cresol at salinity of 46.8‰ and settling time of 0 h to 48 h

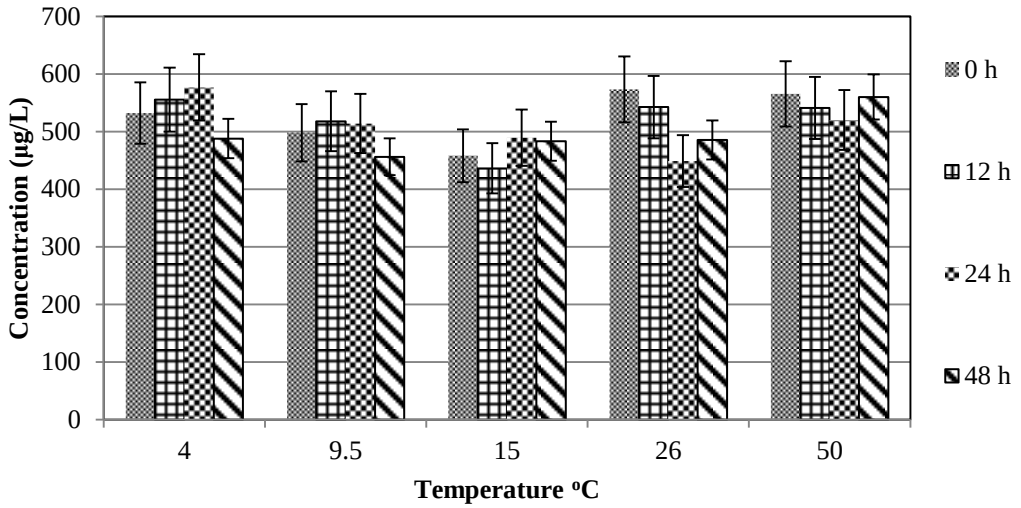

Figure 4.7: Results from settling experiment for p-cresol at salinity of 66.8‰ and settling time of 0 h to 48 h

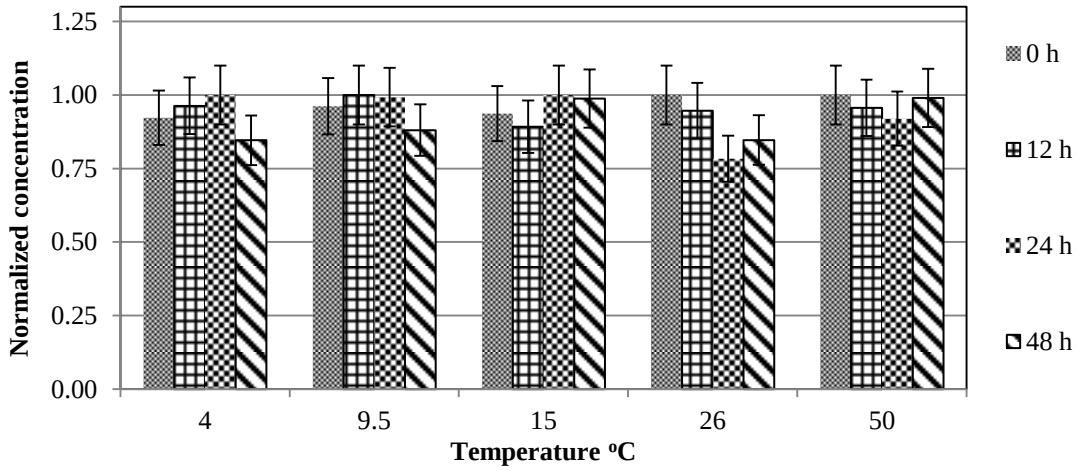

Figure 4.8: Normalized results from settling experiment for p-cresol at salinity of 66.8‰ and settling time of 0 h to 48 h

Within experimental error, there is no change in the concentration of p-cresol in the water phase from 4 ^{o}C and 50 ^{o}C. However, the concentration of p-cresol in the water phase

drops at 70 ^{o}C with 74.5% of the initial p-cresol in the water after 48 h. Therefore approximately 25% of p-cresol may be removed from produced water at 70 ^{o}C using treatment option(s) that targets dispersed oil in produced water.

For the experiments conducted at 66.8‰, there is no change within experimental error in the aqueous concentration of p-cresol from the start of the experiment to 48 h settling time across all temperatures tested. This clearly demonstrates that the contribution to aqueous concentration of p-cresol from the oil droplets (Equation 2.3) in produced water is very small and therefore negligible. Produced water treatment options that remove dissolved fractions (such as dissolved air precipitation or macro porous polymer extraction) will be required to remove phenol and p-cresol from produced water.

For 4-tert-butylphenol, the standard addition plot obtained for experiments conducted at temperatures 9.5 ^{o}C and 26 ^{o}C and 66.8‰ salinity did not give a straight line and was discarded. Both original data and normalized results for 4-tert-butylphenol were presented in figure 4.4.

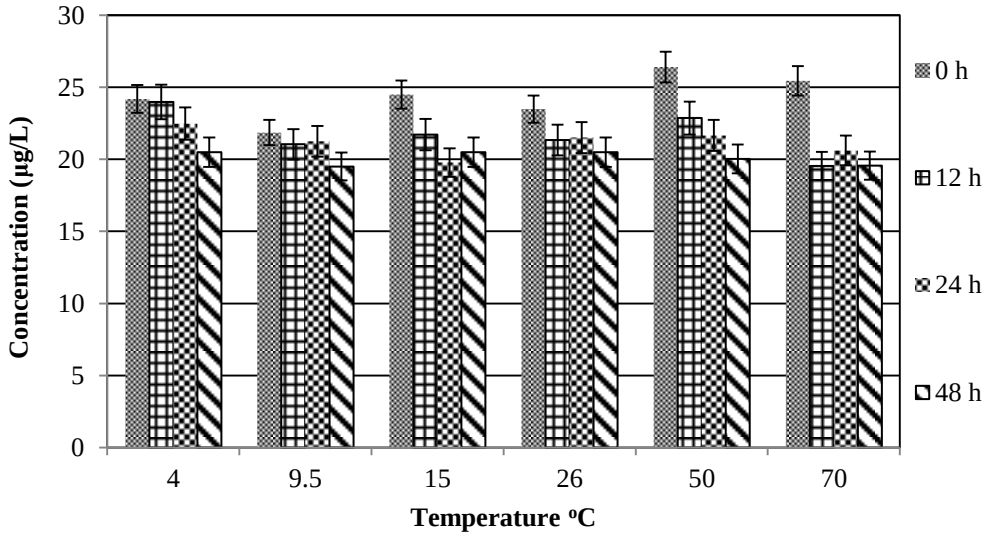

Figure 4.9: Results from settling experiment for 4-tert-butylphenol at salinity of 46.8‰ and settling time of 0 h to 48 h

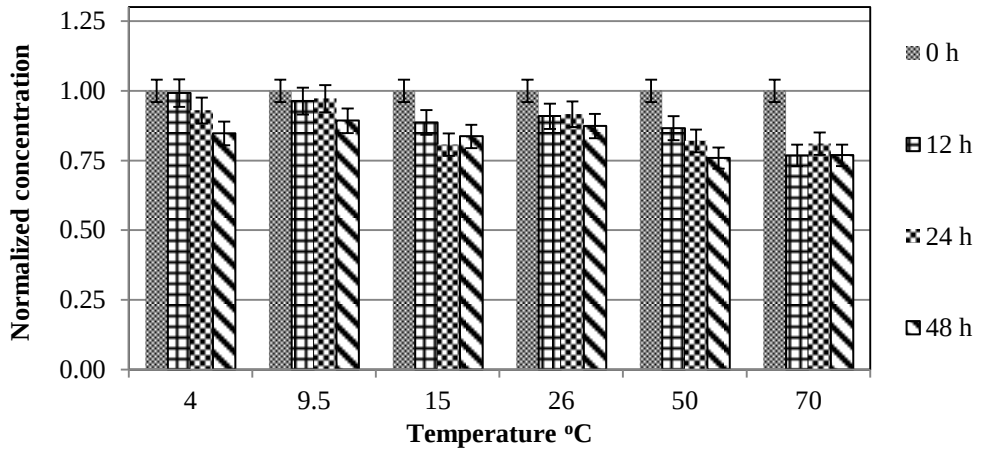

Figure 4.10: Normalized results from settling experiment for 4-tert-butylphenol at salinity of 46.8‰ and settling time of 0 h to 48 h

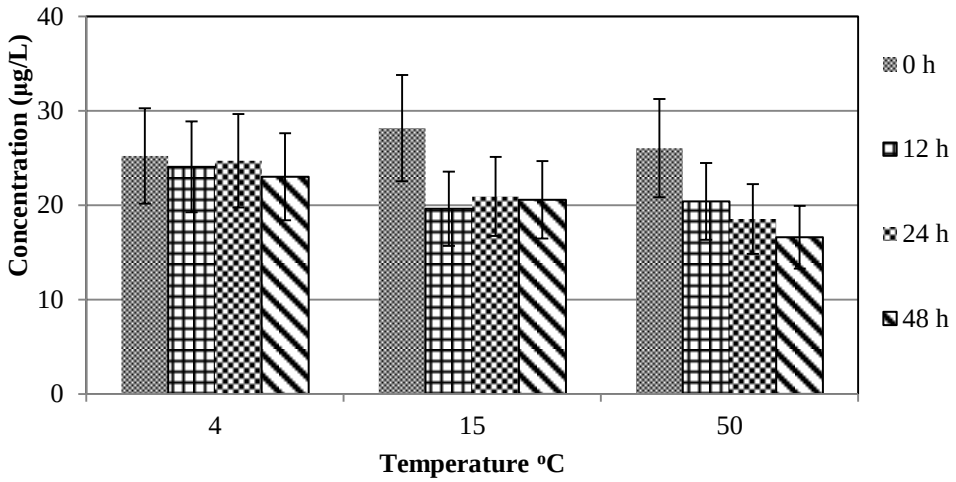

Figure 4. 11: Results from settling experiment for 4-tert-butylphenol at 66.8‰ salinity and settling time of 0 h to 48 h

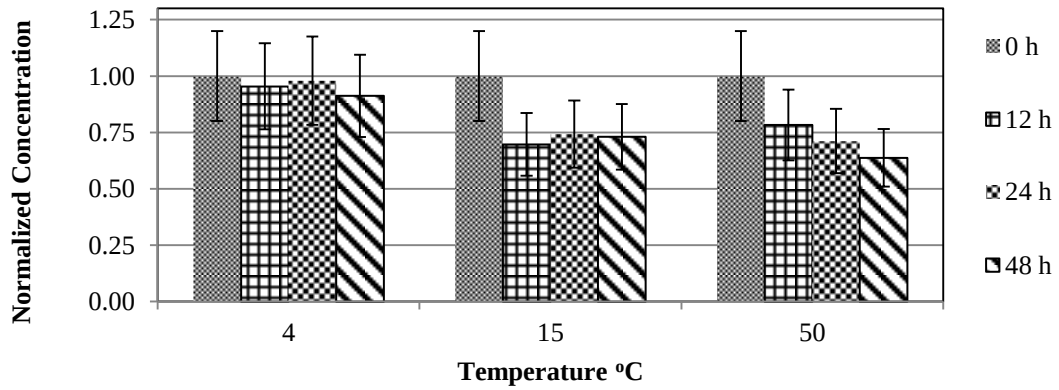

Figure 4.12: Normalized results from settling experiment for 4-tert-butylphenol at 66.8‰ salinity and settling time of 0 h to 48 h

The concentration of 4-tert-butylphenol decreased slightly from the start of the experiment to 48 h settling time. The decrease in the concentration becomes more obvious at higher temperature tested. At 4 ^{o}C approximately 85% of 4-tert-butylphenol was left in the water phase, this is more than the 76% 4-tert-butylphenol left at 70 ^{o}C at

48 h settling time. The concentration of 4-tert-butylphenol decreases slightly with decreasing dispersed oil concentration. Therefore removal of dispersed oil from produced water could reduce the concentration of 4-tert-butylphenol between 15% and 24% at 4 ^{o}C and 70 ^{o}C respectively. Produced water treatment technology, such as MPPE [8], will be more appropriate for removal of 4-tert-butylphenol in produced water.

For the experiment conducted at 4 ^{o}C and 66.8‰ salinity, within experimental error, there is no major change in the aqueous concentration of 4-tert-butylphenol after 48 h settling time. Equilibrium was achieved at 12 h settling time for experiments conducted at 15 ^{o}C and 26 ^{o}C. And the aqueous concentration has decreased to approximately 70% of initial concentration. The effect of salinity is not obvious for 4-tert-butylphenol as there is no major change between experiments conducted at 46.8‰ and 66.8‰ salinities.

4.3 Effect of temperature and salinity on partitioning behavior of naphthalene

The original data and normalized data of naphthalene in the aqueous phase is presented in figure 4.5.

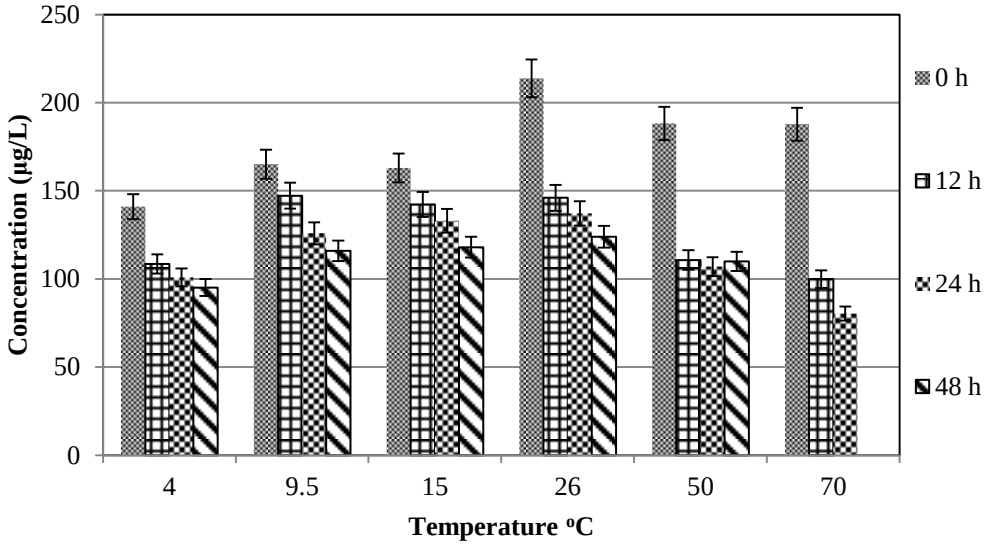

Figure 4.13: Results from settling experiment for naphthalene at 46.8‰ salinity and settling time of 0 h to 48 h

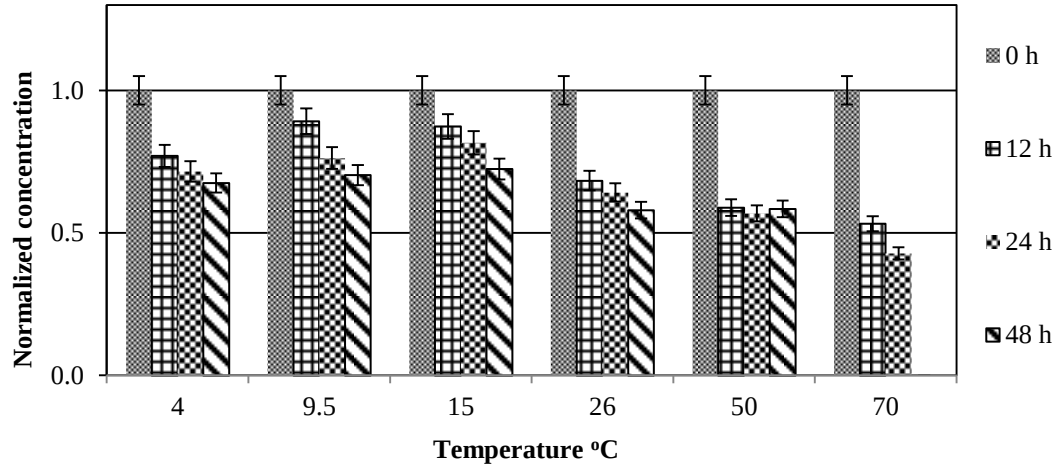

Figure 4.14: Normalized results from settling experiment for naphthalene at 46.8‰ salinity and settling time of 0 h to 48 h

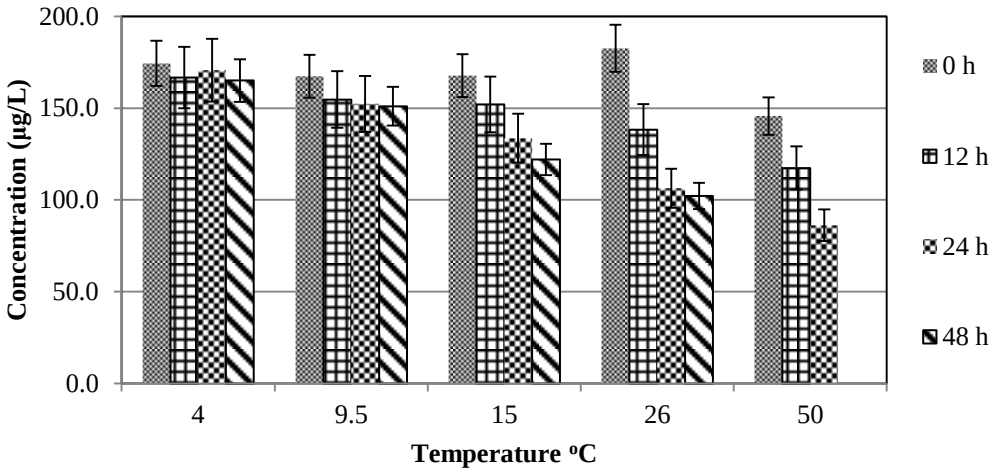

Figure 4.15: Results from settling experiment for naphthalene at 66.8‰ salinity and settling time of 0 h to 48 h

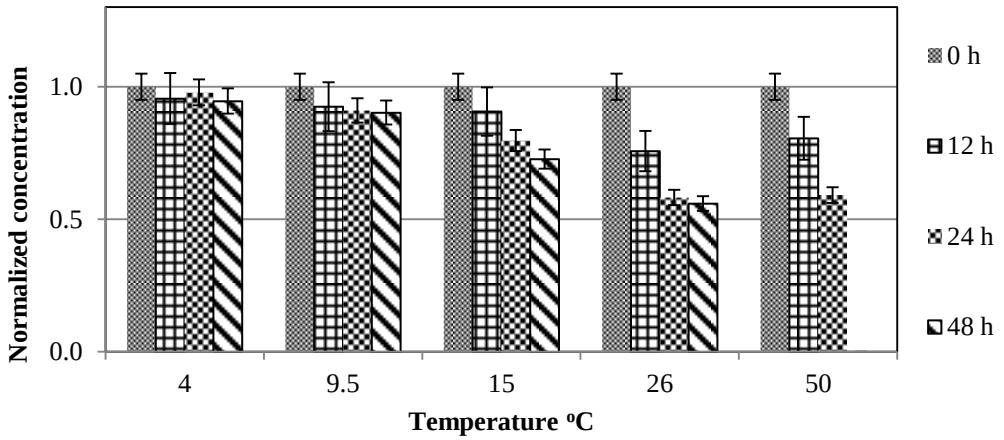

Figure 4. 16: Normalized results from settling experiment for naphthalene at 46.8‰ salinity and settling time of 0 h to 48 h

The concentration of naphthalene in the water phase drops with decreasing dispersed oil concentration at 46.8‰ salinity. After 48 h settling time, the concentration of dispersed oil has reduced to approximately 5 mg/L. The concentration of naphthalene also decreases as the dispersed oil concentration decreases. However, the reduction in the

concentration of naphthalene is not proportional to the concentration of dispersed oil. Approximately 70% of the naphthalene was left in the water phase for experiments conducted at 4 ^{o}C, 9.5 ^{o}C, and 15 ^{o}C. Approximately 58% of naphthalene was left after 24 h for experiments conducted at 26 ^{o}C and 50 ^{o}C. This is can be attributed to the high aqueous solubility (31.7 mg/L) of naphthalene. In the temperature range 4 ^{o}C and 15 ^{o}C only approximately 30% of naphthalene is removed from produced water by reducing dispersed oil concentration to approximately 5 mg/L. At higher temperature, approximately 58% of naphthalene is left in the WAF at 5 mg/L of dispersed oil. Naphthalene may also be volatized from the water phase at higher temperatures. The efficiency of hydrocyclone for oil removal improves with increasing temperature [45, 46]. The combined effect of better oil removal efficiency of hydrocyclone at high temperature and lower concentration of naphthalene in the water phase at higher temperature will aid its removal from produced water.

At 66.8‰ salinity, the matrix becomes more turbid and more dispersed oil was accommodated within the aqueous phase at 50 ^{o}C. After 48 h settling time, the dispersed oil concentration was 6 mg/L at 50 ^{o}C. For the experiments conducted at 66.8‰ salinity, the naphthalene concentration in the water phase was higher than at salinity of 46.8‰. Approximately 94%, 90%, 73%, and 56% of the naphthalene remain in the water phase after 48 h settling time for experiments conducted at 4 ^{o}C, 9.5 ^{o}C, 15 ^{o}C, and 26 ^{o}C respectively. Again the concentration of naphthalene in the water phase decreases with increasing temperature.

4.4 Effect of temperature and salinity on partitioning behavior of phenanthrene

The aqueous concentration of phenanthrene is strongly related to the dispersed oil concentration as shown in Figure 4.5.

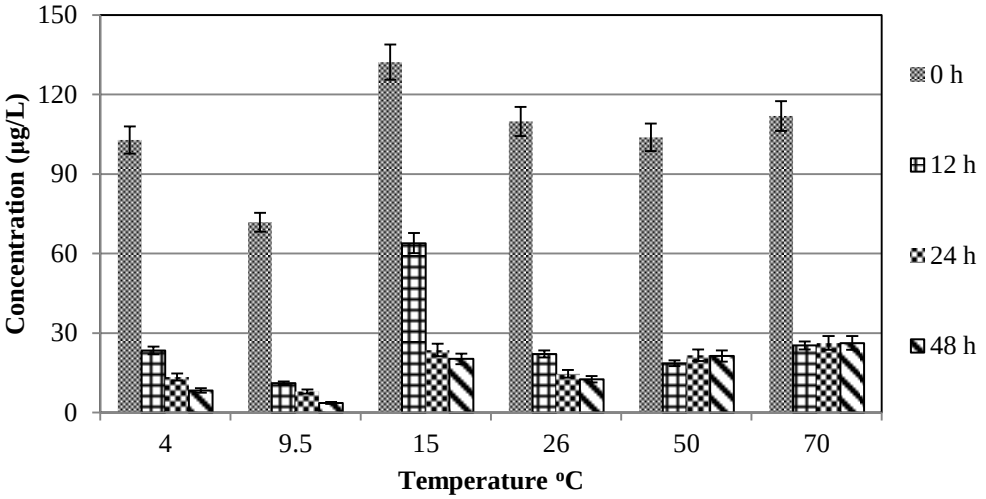

Figure 4.17: Results from settling experiment for phenanthrene at 46.8‰ salinity and settling time of 0 h to 48 h

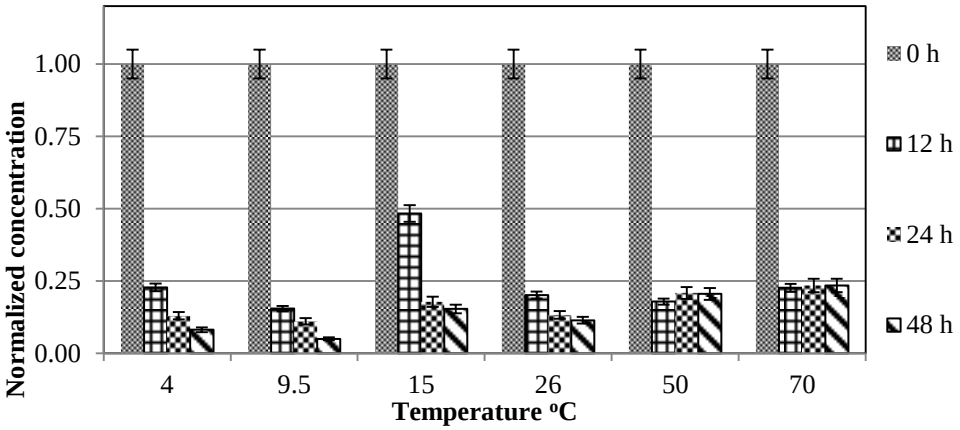

Figure 4.18: Results from settling experiment for phenanthrene at 46.8‰ salinity and settling time of 0 h to 48 h

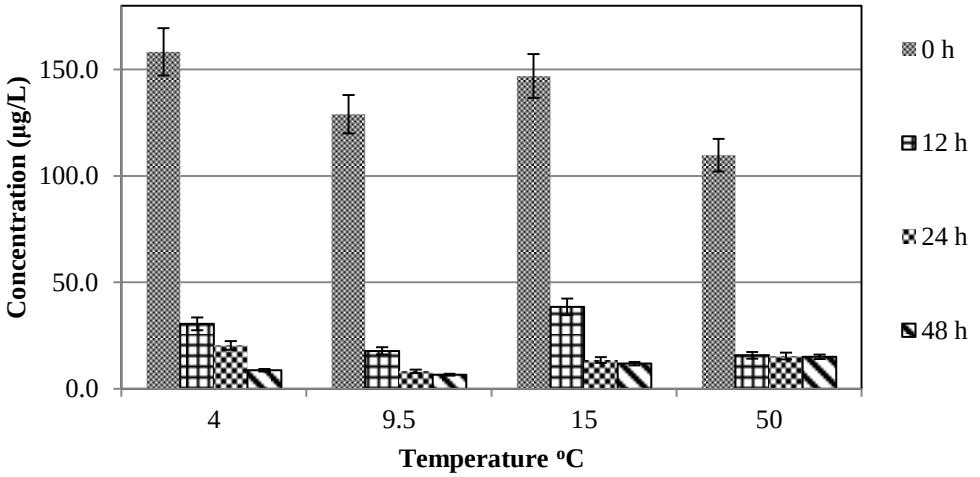

Figure 4.19: Results from settling experiment for phenanthrene at 66.8‰ salinity and settling time of 0 h to 48 h

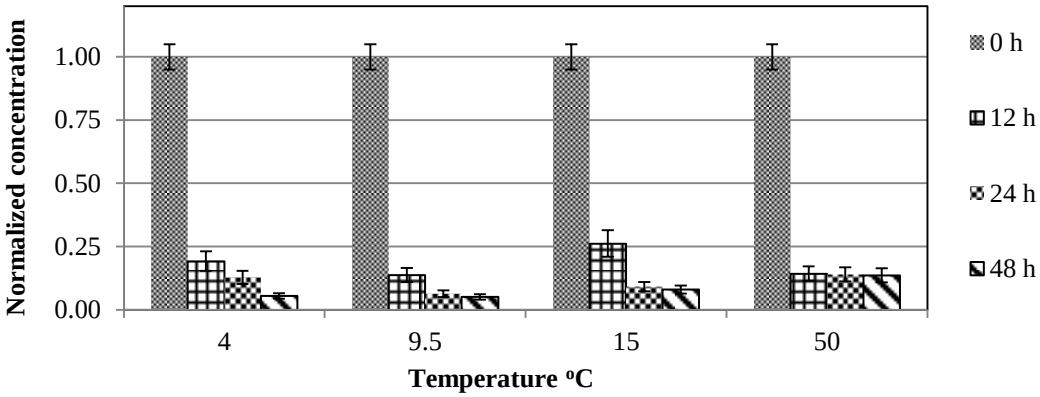

Figure 4.20: Normalized results from settling experiment for phenanthrene at 66.8‰ salinity and settling time of 0 h to 48 h

At 4°C, the concentration of phenanthrene after 48 h has dropped to 8% of initial concentration in the water phase. This is largely due to the low water solubility of phenanthrene. However, as the temperature increases, 23% phenanthrene was retained in the water phase at 70 °C and equilibrium was achieve after 12 h for experiments

conducted 50 ^{o}C and 70 ^{o}C even though the dispersed oil concentration in the water continue to decrease with time. Whitehouse (1984) reported that the solubility of phenanthrene at 4.6 ^{o}C and 36.1‰ salinity is 1.36 µmol/L, this increased to 4.54 µmol/L at 25.3 ^{o}C. It can be inferred that the concentration of phenanthrene in the water phase is a function of dispersed oil concentration and temperature. Technologies (i.e. hydrocyclones) geared towards removal of dispersed oil will have higher potential for removal of phenanthrene from produced water. At 5 mg/L of dispersed oil concentration, 92% and 76.5% of phenanthrene would have been removed from the water at 4 ^{o}C and 70 ^{o}C respectively. The concentration of phenanthrene in the water phase tends to increase with increasing temperature. It further shows that phenanthrene is more resistant to vaporization compared to naphthalene. The vapor pressure of phenanthrene at 70 ^{o}C is 3.932 Pa as compare to 332.1 Pa for naphthalene at the same temperature [47]. At 4 ^{o}C, approximately 5% of phenanthrene remains in solution at 66.8‰ salinity compare to 8% at 46.8‰ salinity. This is likely as a result of salting out effect of PAHs with increasing salinity. The concentration of phenanthrene in the water also increases with increasing temperature. This shows that more phenanthrene partition into the water phase with increasing temperature. The log K_{ow} for phenanthrene decreases with increasing temperature indicating that increase in temperature favors water solubility in an aqueous system.

4.5 Effect of temperature and salinity on the partitioning of fluorene

The concentration of fluorene in the produced water tested was relatively small as compared to phenanthrene and naphthalene. The original data normalized result for fluorene is presented in Figure 4.7.

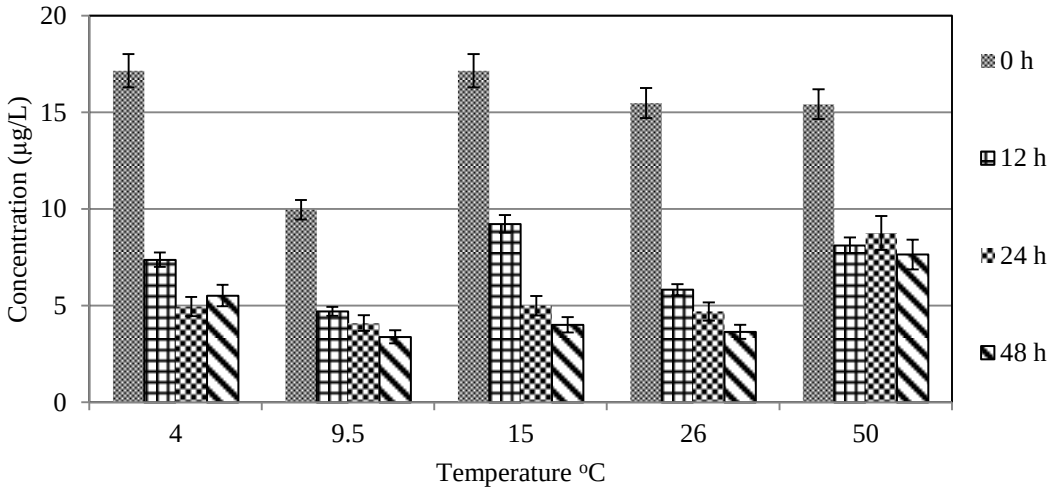

Figure 4.21: Results from settling experiment for fluorene at 46.8‰ salinity and settling time of 0 h to 48 h

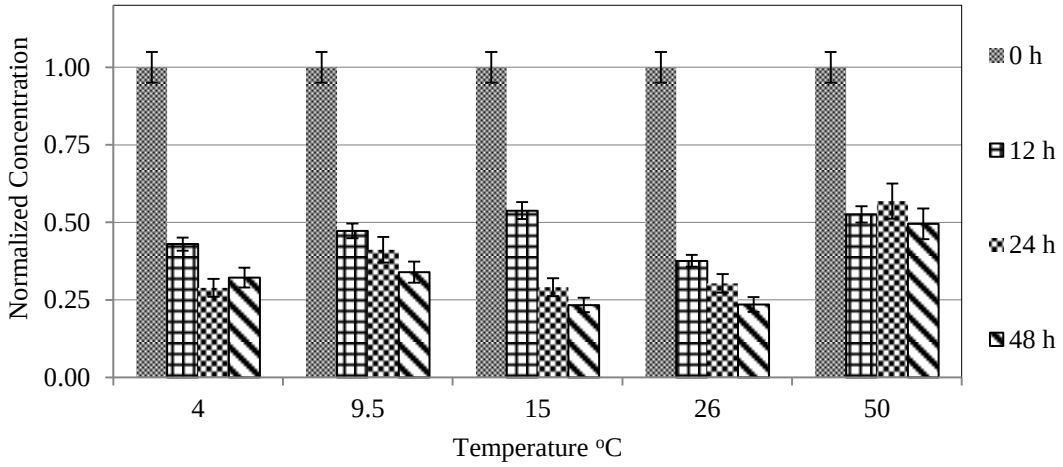

Figure 4.22: Normalized results from settling experiment for fluorene at 46.8‰ salinity and settling time of 0 h to 48 h

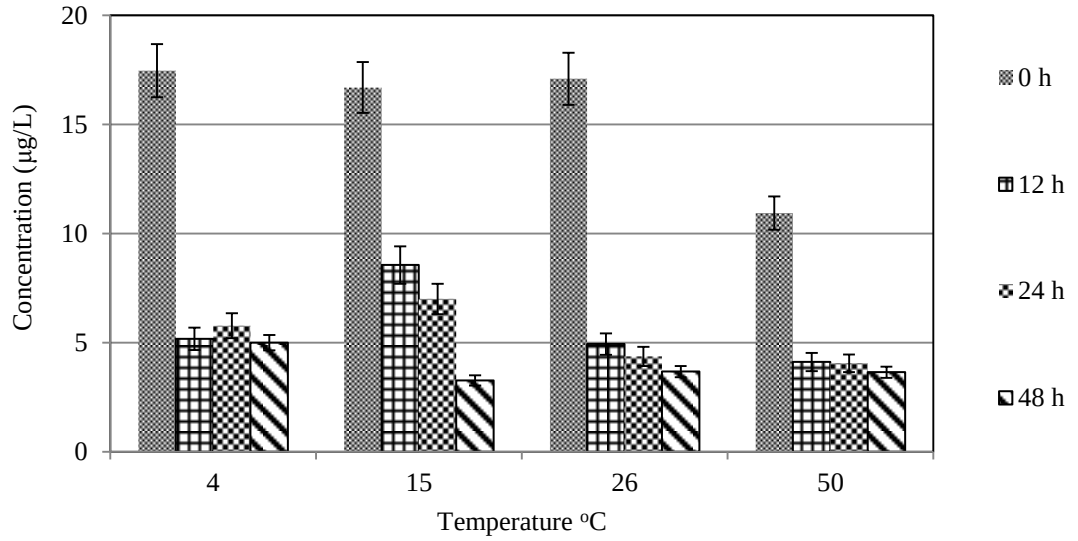

Figure 4.23: Results from settling experiment for fluorene at 66.8‰ salinity and settling time of 0 h to 48 h.

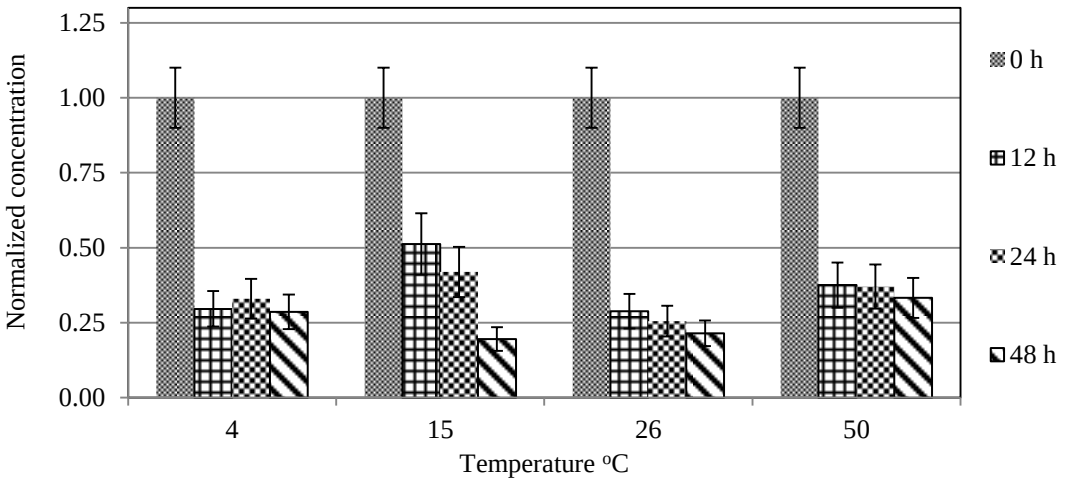

Figure 4.24: Normalized results from settling experiment for fluorene at 66.8‰ salinity and settling time of 0 h to 48 h

The concentration of fluorene drops as the settling experiment progresses from the start to 48 h across all temperatures tested. This clearly shows that the concentration of

fluorene decreases as the dispersed oil concentration decreases. This indicates that fluorene partition into the oil phase as the experiment progresses. For the experiment conducted at salinity of 46.8‰, the percentage of fluorene left after 48 h in the water phase at 4 ^{o}C and 9.5 ^{o}C are 32% and 34% respectively. This implies that the fluorene concentration in the water phase is largely impacted by the dispersed oil concentration. At 50 ^{o}C, more fluorene is retained in the water phase with 49.5% left after 48 h settling time. This implies that more fluorene increasingly partition into the water phase as the temperature is increased. Therefore, removal of dispersed oil in produced water treatment system at low temperature have greater propensity to remove fluorene from the water than at 50 ^{o}C.

For the experiments carried out at 66.8‰, the concentration of fluorene in the water phase increases with increasing temperature for experiments conducted at 9.5 ^{o}C, 15 ^{o}C, 26 ^{o}C, and 50 ^{o}C. For the test conducted at 4 ^{o}C, the percentage of fluorene left in the water is 28.8%, this is higher than 19.6% and 21.5% recorded for test conducted at 9.5 ^{o}C and 26 ^{o}C respectively. Again this might be as a result of higher dispersed oil concentration recorded at 4 ^{o}C. The differences in the percentage of fluorene left after 48 h for the two salinities tested can be attributed to salting out. For experiment conducted at 50 ^{o}C, 49.6% fluorene was left in the water at 46.8‰ salinity as compared to 33.3% fluorene in the water at 66.8% salinity. This effect was observed for all the temperatures tested. It can be inferred from the results obtained that solubility of fluorene in produced water increases with increasing temperature and decreases with increasing salinity. Furthermore, a greater percentage of fluorene in produced water are associated with the

dispersed oil. Reduction in dispersed oil concentration will greatly reduce the concentration of PAHs in produced water.

4.6 Reduction of dispersed oil concentration versus analyte concentration

According to the model presented by Page et al. (2000) [17], the concentration of analyte is controlled by two mechanism; the aqueous solubility of the analyte (governed by Raoult's law, which is likely oversimplified for this complex matrix) and presence of micro droplets of oil. It can inferred from the results presented above that for compounds with high water solubility, such as phenol, the solubility is the main driving factor for analyte concentration in WAF. For higher PAHs that are only slightly soluble in water the micro oil droplets becomes the main driving factor. A summary of analytes concentration as the dispersed oil was reduced from 116 mg/L to 6 mg/L for experiment conducted at 66.8‰ salinity and 26 ^{o}C is presented below.

Table 4.3: Concentration of contaminants in produced water at various concentration of dispersed oil for experiment conducted at 66.8‰ salinity and 26 ^{o}C

Dispersed oil	116 mg/L	17 mg/L (85.3% reduction)		8 mg/L (93.1% reduction)		6 mg/L (94.8% reduction)	
Analytes	µg/L	µg/L	% reduction	µg/L	% reduction	µg/L	% reduction
Phenol & p-cresol	1445	1426	none	1378	none	1392	none
Naphthalene	183	138	24	106	42	102	44
Fluorene & Phenanthrene	164	43	74	18	89	15	91
Pyrene	7.9	4.2	46	2.0	75	1.5	81

From the Table 4.3 above, the concentration of dispersed oil dropped drastically from average 116 mg/L to 17 mg/L representing settling time zero and 12 h respectively. Phenol and p-cresol shows no change in concentration as the dispersed oil was reduced by 95%. When dispersed was reduced by 85%, naphthalene concentration in the WAF was reduced by 24%. This is lower than 74% reduction in the concentration of fluorine and phenanthrene. At the end of the experiment, dispersed oil has been reduced by 94.8%. Whereas phenol shows no appreciable change in concentration, pyrene concentration has reduced by 81%. The result presented above is comparable to data presented by Faksness et al. (2004) in Table 4.4. Faksness et al. (2004) conducted partitioning experiments on offshore oil and gas produced water, but there was no mention of temperature. So it is safe to assume that the experiment was carried out at ambient temperature. A similar trend was observed in the data presented in Table 4.3 and literature values in table 4.4

Table 4.4: Estimated concentration of EIF components in produced water at various concentrations of dispersed oil (reproduced from Faksness et al. 2004)

Dispersed oil	40 mg/L	20 mg/L (50% reduction)		5 mg/L (87.5% reduction)	
EIF groups	µg/L	µg/L	% reduction	µg/L	% reduction
Naphthalenes	1312	991	24	751	43
2-3 Ring PAH	205	122	40	60	71
4-6 Ring PAH	3.17	1.77	44	0.71	78
C0 -C3 Phenols	3521	3518	none	3516	none
C4 -C5 Phenols	153	143	6	136	11
C6 -C9 Phenols	2.47	1.37	45	0.55	78

This work by Faksness et al. 2004 provides the first data on partitioning of phenols and PAHs in produced water. However, the study did not cover the effect of temperature and

salinity on the partitioning pattern of constituent of produced water. A similar partitioning experiment has been conducted on pure sample by Brian Whitehouse in 1984, but this is quite different from a complex matrix such as produced water. This work is the only work in literature that attempts to quantify the effect of temperature and salinity on the partitioning pattern of phenol and selected PAHs in produced water using the settling experiment.

Chapter 5: Steady State Modeling and Simulation of Produced Water Treatment System

5.1 Petroleum fluid characterization

The produced water was simulated by mixing crude oil with water which has been spiked with phenol, p-cresol, naphthalene, phenanthrene, fluorene, and pyrene. Figure 5.1 of shows the HYSYS produced water process flow diagram.

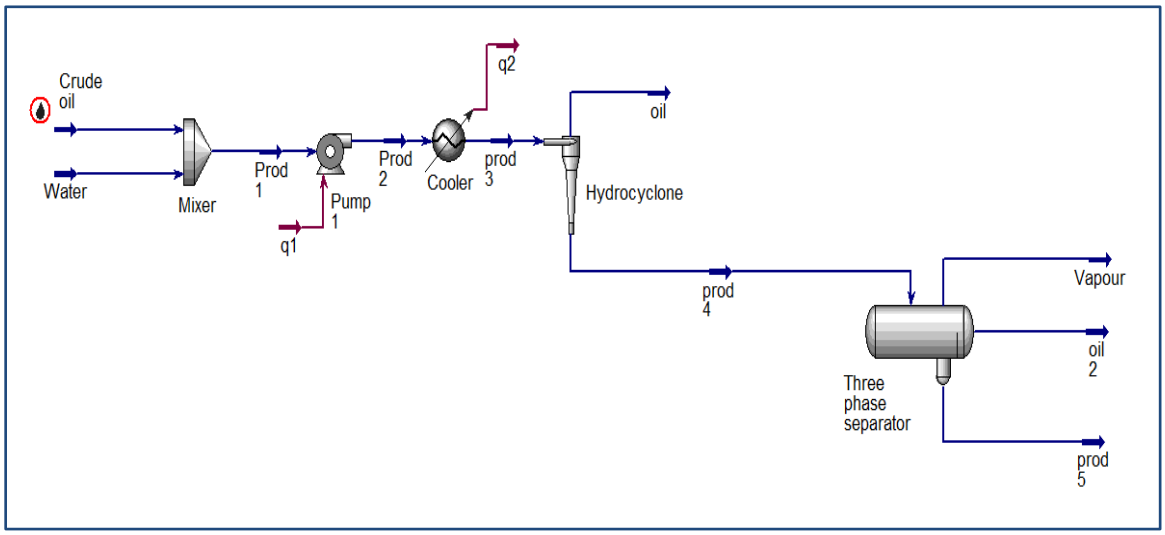

Figure 5.1: Produced water process flow diagram in Aspen HYSYS V8.6

Table 3.5 of chapter three shows the concentration of analytes in the water. The petroleum fluid was characterized using the crude oil assay from Terra Nova oilfield offshore Newfoundland and Labrador [48]. The assay data used to characterize the crude oil are presented in table 5.1. HYSYS converts this assay data of crude oil into a series of distinct hypothetical components which in turn was used to predict thermodynamics and transport properties. The SRK-Twu fluid package was used to predict the thermodynamic

and transport properties of the fluid. The popular Peng Robinson fluid package is not suitable for p-cresol and pyrene.

Table 5.1: Assay data used in characterizing the petroleum fluid (Bulk properties, API gravity, and TBP distillation)

Bulk Properties	
API Gravity	33.2
Density @15 ^{o}C (g/cm^{3})	0.86
Total Sulphur (% wt)	0.50
Molecular Weight (g/mole)	302
Viscosity @ 20°C (cSt)	13.6
Viscosity @ 40°C (cSt)	7.38

API Gravity Assay	
Cumulative yield (%wt)	API Gravity
1.4	87.2
3.8	66.7
7.5	52.9
16.1	45.8
24.1	39.2
32.8	35.3
41.6	31.6
50.2	29.0

TBP Distillation Assay		
Temperature ^{o}C	Cumulative yield (%wt)	Sulfur
65	1.4	0.000
100	3.8	0.001

150	7.5	0.002
200	16.1	0.007
250	24.1	0.034
300	32.8	0.141
350	41.6	0.331
370	50.2	0.451

Figure 5.2 presents the true boiling point (TBP) distillation curve of the crude oil. TBP separates the components of the crude oil according to boiling points. The crude output blend composition by mass fraction is presented in table 5.2. The crude comprises of hypothetical components which represents compounds with normal boiling point in the range of -6 ^{o}C to 752 ^{o}C.

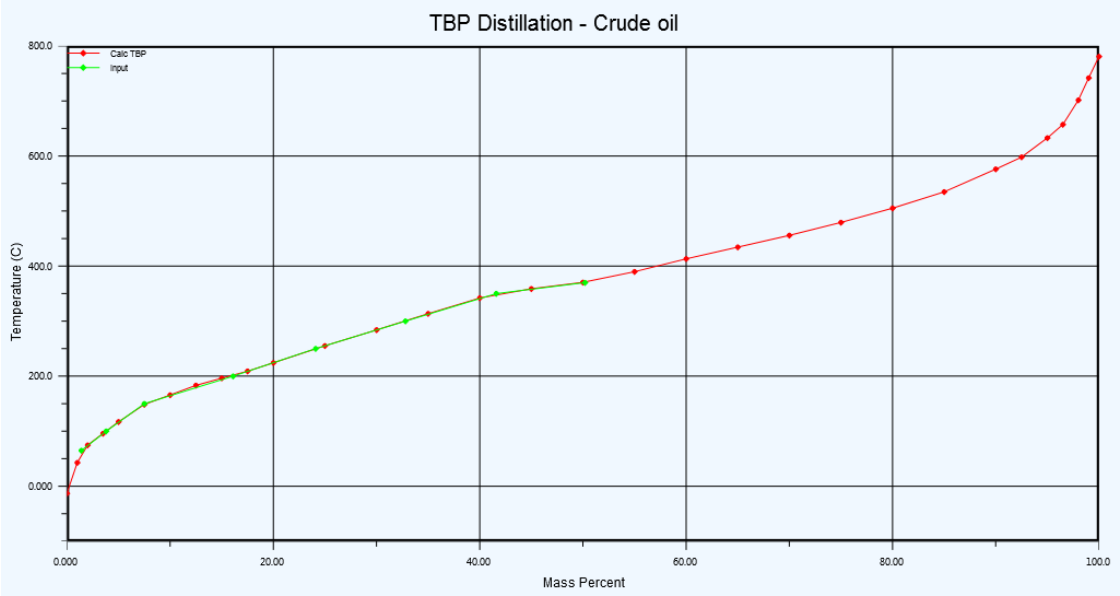

Figure 5.2: True boiling point distillation curve of the crude oil

Table 5.2: Simulated crude oil

Hydrocarbons	**Mass fraction**	**Hydrocarbons**	**Mass fraction**
NBP[0]-6*	2.29E-03	NBP[0]283*	2.43E-02
NBP[0]8*	2.40E-03	NBP[0]296*	2.34E-02
NBP[0]23*	2.74E-03	NBP[0]310*	2.25E-02
NBP[0]38*	2.98E-03	NBP[0]324*	2.30E-02
NBP[0]49*	1.88E-03	NBP[0]338*	2.59E-02
NBP[0]63*	5.67E-03	NBP[0]353*	4.25E-02
NBP[0]78*	8.05E-03	NBP[0]364*	6.01E-02
NBP[0]90*	9.96E-03	NBP[0]378*	3.38E-02
NBP[0]104*	9.55E-03	NBP[0]392*	2.99E-02
NBP[0]118*	9.84E-03	NBP[0]407*	2.94E-02
NBP[0]132*	1.01E-02	NBP[0]420*	3.24E-02
NBP[0]146*	1.36E-02	NBP[0]441*	6.50E-02
NBP[0]159*	2.21E-02	NBP[0]468*	5.92E-02
NBP[0]173*	1.78E-02	NBP[0]496*	5.18E-02
NBP[0]187*	2.35E-02	NBP[0]523*	4.60E-02
NBP[0]200*	2.96E-02	NBP[0]551*	3.53E-02
NBP[0]214*	2.25E-02	NBP[0]580*	2.95E-02
NBP[0]228*	2.16E-02	NBP[0]605*	2.36E-02
NBP[0]241*	2.22E-02	NBP[0]635*	1.71E-02
NBP[0]255*	2.31E-02	NBP[0]674*	2.52E-02
NBP[0]269*	2.38E-02	NBP[0]752*	1.49E-02

The crude oil was mixed with water to mimic produced water. The phase diagram of the oil is shown in Figure 5.3.

Figure 5.3: PT phase diagram of the crude oil

The composition of the water stream by mass fraction is shown in table 5.3. The water (spiked with analytes) and the crude oil were then mixed together with the aid of mixer to mimic produced water represented by Stream Prod 1.

Table 5.3: Composition of water spiked with analytes based on produced water analysis

Components	**Mass fraction**
H_2O	9.99E-01
Phenol	1.00E-06
p-Cresol	7.00E-07
Naphthalene	2.00E-07
Fluorene	1.50E-08
Phenanthrene	1.50E-07

5.2 Material and energy flow

Tables 5.4 to 5.6 show the flow conditions in and out of the mixer, hydrocyclone, and three phase separator respectively. Stream Prod 1 represents simulated produced water i.e. mixture of crude oil and water exiting the mixer.

Table 5.4: Material and energy flow into and out of the mixer

Name	**Crude oil**	**Water**	**Prod 1**
Vapor	4.7E-03	0.0	0.0
Temperature [C]	75.0	70.0	70.0
Pressure [kPa]	203.0	304.0	203.0
Molar Flow [kgmole/h]	4.18E-02	3.05E+03	3.05E+03
Mass Flow [kg/h]	1.06E+01	5.49E+04	5.49E+04
Std Ideal Liq Vol Flow [m3/h]	1.23E-02	5.50E+01	5.50E+01
Molar Enthalpy [kJ/kgmole]	-5.19E+05	-2.82E+05	-2.82E+05
Molar Entropy [kJ/kgmole-C]	46.4E+01	6.54E+01	6.54E+01
Heat Flow [kJ/h]	-2.17E+04	-8.61E+08	-8.61E+08

Table 5.5: Material and energy flow in and out of the hydrocyclone

Name	**prod 3**	**oil**	**prod 4**
Vapor	0.0	0.0	0.0
Temperature [C]	4.2	4.2	4.3
Pressure [kPa]	2.2E+3	0.90E+3	1.7E+3
Molar Flow [kgmole/h]	3.1E+3	0.10E+3	2.9E+3
Mass Flow [kg/h]	54.9E+3	2.14E+3	52.8E+3
Std Ideal Liq Vol Flow [m3/h]	55.0	2.14	52.9
Molar Enthalpy [kJ/kgmole]	-2.9E+5	-2.9E+5	-2.9E+5
Molar Entropy [kJ/kgmole-C]	48.4	48.5	48.5
Heat Flow [kJ/h]	-87.6E+7	-3.40E+7	-84.2E+7

Table 5.6: Material and energy flow in and out of the three phase separator

Name	**prod 4**	**oil 2**	**Vapor**	**prod 5**
Vapour	0.0	0.0	1.0	0.0
Temperature [C]	4.3	4.3	4.3	4.3
Pressure [kPa]	1.7E+3	1.7E+3	1.7E+3	1.7E+3
Molar Flow [kgmole/h]	2.9E+3	2.1E-2	0.0	2.9E+3
Mass Flow [kg/h]	5.3E+4	5.4	0.0	5.3E+4
Std Ideal Liq Vol Flow [m^3/h]	52.9	6.30E-3	0.0	52.9
Molar Enthalpy [kJ/kgmole]	-2.9E+5	-5.8E+5	-1.5E+5	-2.9E+5
Molar Entropy [kJ/kgmole-C]	48.5	345	118	48.5
Heat Flow [kJ/h]	-8.4E+8	-1.2E+4	0.0	-8.4E+8

5.3 Feed Composition

In this model, priority will be placed on the hydrocyclone since that is where major part of the oil in water is removed. The flow compositions will be analyzed in detail and simulation will center on the hydrocyclone. Table 5.7 shows the composition of the feed into the hydrocyclone (prod 3) by mass fraction. See appendix A for composition of streams prod 4, oil, prod 5, and oil 2. The concentration of dispersed oil in stream prod 3 is 227 ppm as simulated by the hydrocyclone.

Table 5.7: Composition of feed into the hydrocyclone

Hydrocarbons	**Mass fraction**	**Hydrocarbons**	**Mass fraction**
H_2O	0.99	NBP[0]241*	4.26E-06
Phenol	1.00E-06	NBP[0]255*	4.42E-06
p-Cresol	7.00E-07	NBP[0]269*	4.57E-06
Naphthalene	2.00E-07	NBP[0]283*	4.67E-06
Fluorene	1.50E-08	NBP[0]296*	4.49E-06
Phenanthrene	1.50E-07	NBP[0]310*	4.30E-06
Pyrene	1.00E-08	NBP[0]324*	4.41E-06
NBP[0]-6*	4.39E-07	NBP[0]338*	4.96E-06
NBP[0]8*	4.60E-07	NBP[0]353*	8.15E-06
NBP[0]23*	5.26E-07	NBP[0]364*	1.15E-05
NBP[0]38*	5.70E-07	NBP[0]378*	6.47E-06
NBP[0]49*	3.60E-07	NBP[0]392*	5.73E-06
NBP[0]63*	1.09E-06	NBP[0]407*	5.64E-06
NBP[0]78*	1.54E-06	NBP[0]420*	6.21E-06
NBP[0]90*	1.91E-06	NBP[0]441*	1.25E-05
NBP[0]104*	1.83E-06	NBP[0]468*	1.14E-05

NBP[0]118*	1.89E-06	NBP[0]496*	9.93E-06
NBP[0]132*	1.94E-06	NBP[0]523*	8.81E-06
NBP[0]146*	2.60E-06	NBP[0]551*	6.76E-06
NBP[0]159*	4.24E-06	NBP[0]580*	5.65E-06
NBP[0]173*	3.40E-06	NBP[0]605*	4.53E-06
NBP[0]187*	4.51E-06	NBP[0]635*	3.28E-06
NBP[0]200*	5.66E-06	NBP[0]674*	4.83E-06
NBP[0]214*	4.31E-06	NBP[0]752*	2.85E-06
NBP[0]228*	4.13E-06		

5.4 Simulation results

All equipment employed for separating oil from water uses Stoke's law as the fundamental principle. Stoke's law states that the oil in water rising velocity is a function of the square of oil droplet diameter, density difference between the oil and water, and fluid viscosity as shown in Equation 5.1 [49].

$$V_r = \frac{gd^2(\rho_w - \rho_o)}{18\mu} \tag{5.1}$$

V_r is the rising velocity of the oil, g is the acceleration due to gravity, d is the oil droplet diameter, ρ_w is the density of water, ρ_o is the density of oil, and μ is the viscosity of water. The oil droplet diameter has the greatest impact on the rising velocity of oil to the surface. Rising velocity reduces as the oil droplet diameter decreases. Small oil droplets are accommodated within the water phase. Therefore, it is more difficult to separate small oil droplet from produced water. Oil droplet diameter is influenced mainly by the

activities upstream of the inlet separators; shearing and coalescing of the fluids in the pipeline, valves, risers determine the oil droplet diameter and distribution [49]. Moreover, the type equipment employed, the flow rate of the fluid, the temperature, and the intensity of the turbulence affects the oil droplet distribution and diameter. The density difference between the oil and water as well as the viscosity of water is greatly influenced by temperature [35, 50, 51]. Decrease in temperature increases the viscosity of water thereby reducing the rising velocity hence reducing the separation of oil from water [51, 52].

Oil removal efficiency of hydrocyclone is calculated using the widely used definition of oil separation efficiency presented in equation 5.2 [49]

$$E_{ff} = \left[1 - C_o / C_i\right] \times 100\% \tag{5.2}$$

E_{ff} is the oil removal efficiency (%), C_o is the dispersed oil concentration in the water outlet stream (mg/L), and C_i is the dispersed oil concentration in the water inlet stream (mg/L)

5.4.1 Effect of oil droplet distribution on efficiency of hydrocyclone

Oil droplet distribution has the greatest impact on the oil-water separation efficiency of the hydrocyclone [53]. Figure 5.4 shows the separation performance of the hydrocyclone as a function of oil droplet distribution (median oil diameter)

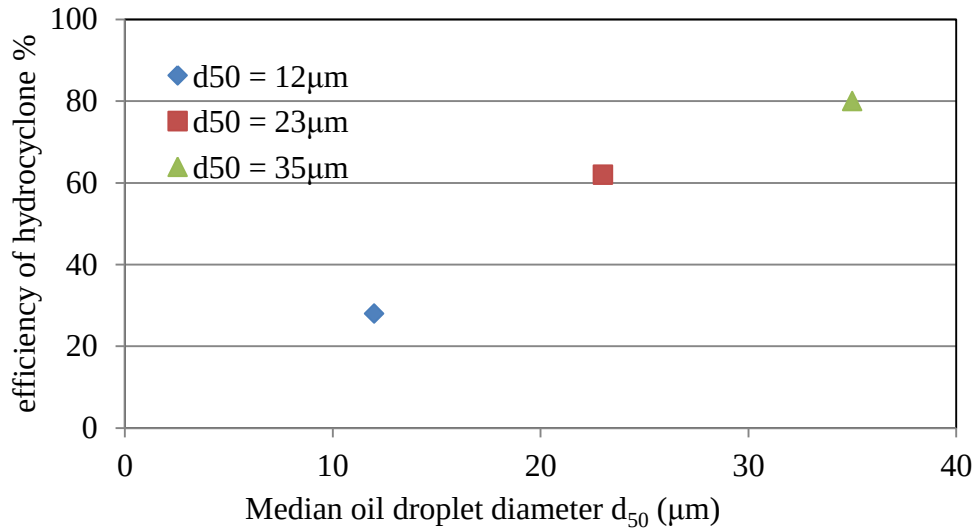

Figure 5.4: Effect of oil droplet size on efficiency of hydrocyclone

Figure 5.4 shows that oil-water separation efficiency increase with increasing oil droplet size. Larger oil droplets coalesce faster than smaller oil droplets and the rising velocity increases as the oil diameter increases as shown in Equation 5.1. The hydrocyclone operates at 80% efficiency at d50 of 35 µm. This efficiency dropped to 28% at d50 of 12 µm. Hydrocyclones are generally not suitable for removal of oil droplet diameter below 10 µm [54].

5.4.2 Effect of temperature on the efficiency of hydrocyclone

From the model developed, feed temperature has great impact on the efficiency of hydrocyclone. Typical temperature of produced water entering into the hydrocyclone is between 70 ^{o}C and 80 ^{o}C [35, 54] and discharge at the end of produced water treatment train at ambient temperature. Therefore feed temperature into the hydrocyclone was

varied from 4 ^{o}C to 80 ^{o}C. The plot of feed (prod 3) temperature into hydrocyclone versus the oil removal efficiency of hydrocyclone is shown in Figure 5.3.

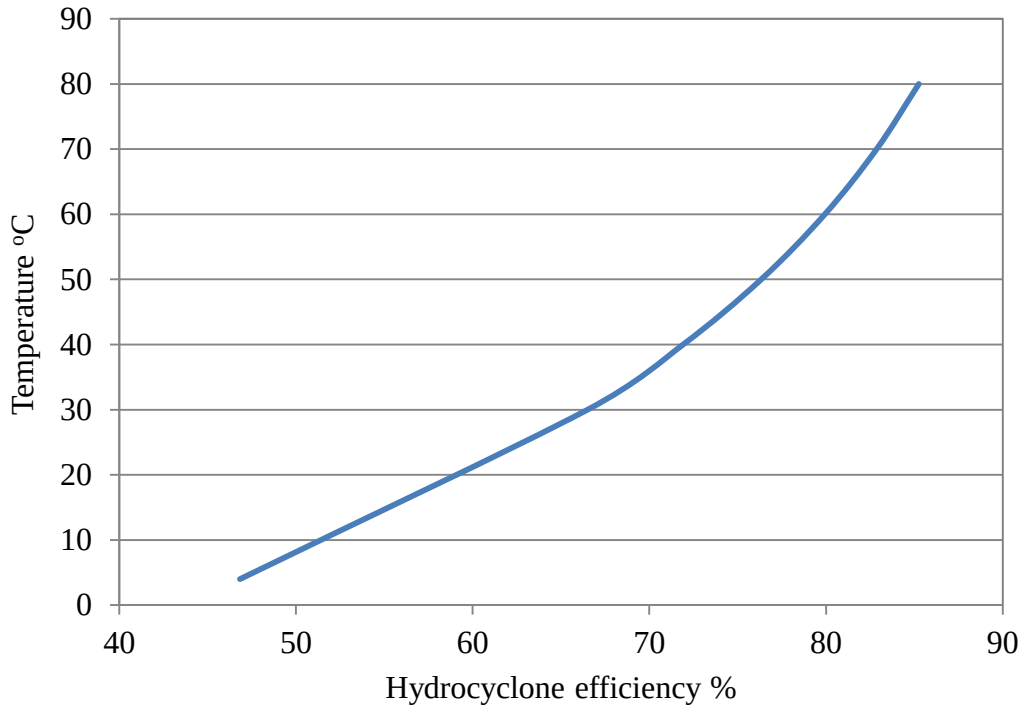

Figure 5. 5: Temperature versus efficiency of modeled hydrocyclone

The efficiency of hydrocyclone increases with increasing temperature. The impact of temperature on the oil removal efficiency of hydrocyclone is substantial. At 4 ^{o}C the efficiency of the hydrocyclone is 47% as compared to 85% efficiency at 80 ^{o}C. As temperature is reduced, the density of the dispersed oil increases causing more oil to flow to the underflow stream thereby reducing the oil removal efficiency of the hydrocyclone [49]. The optimum operating temperature of the hydrocyclone is 80 ^{o}C and it is beneficial to maintain the feed temperature at 80 ^{o}C for maximum recovery of dispersed oil. The

concentration of oil in produced water exiting the hydrocyclone as underflow also decreases with increasing temperature as presented in Figure 5.4

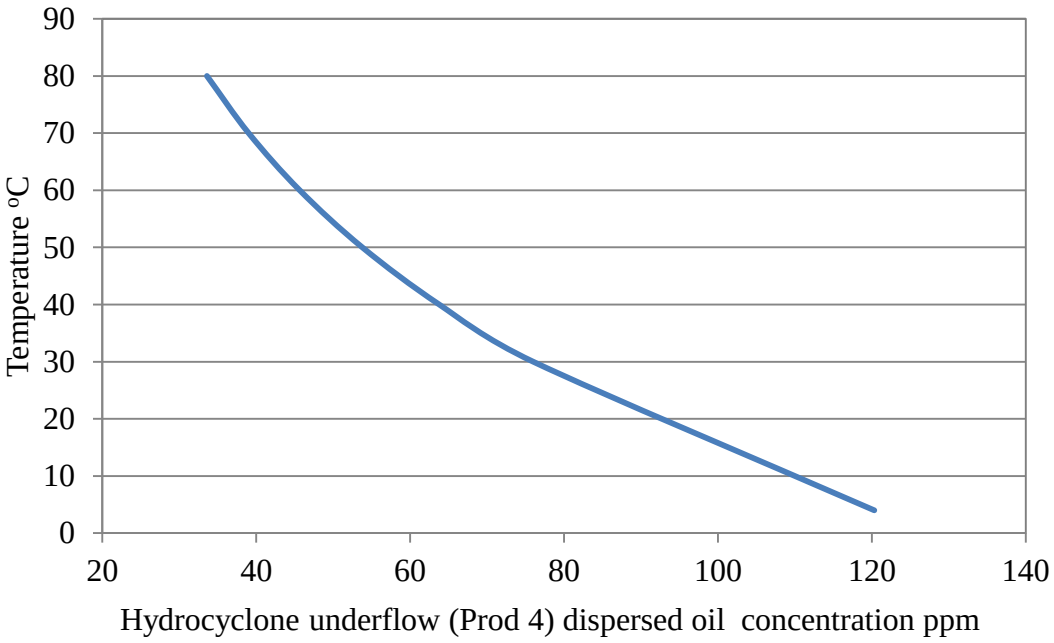

Figure 5.6: Oil concentrations in produced water underflow from hydrocyclone at varying temperature

The dispersed oil concentration in produced water effluent from hydrocyclone increases with decreasing temperature as the efficiency of the hydrocyclone decreases. At 30 ^{o}C the dispersed oil concentration in the produced water is 76 ppm as compared to 46 ppm at 60 ^{o}C and 34 ppm at 80 ^{o}C. In colder climate where ambient temperatures drops below 0 ^{o}C, maintaining the fluid temperature may require additional energy (a challenge in remote offshore location) absence of which the fluid temperature will likely drop thereby impacting negatively on the performance of treatment system.

5.5 Partitioning of component of produced water between oil phase and water phase

It has been demonstrated that temperature has direct impact on the dispersed oil concentration in the hydrocyclone underflow produced water as shown in Figure 5.2. It is equally important to know how compounds considered toxic in the marine environment partition between the oil phase and water phase. That is how much of these compounds of interest are associated with dispersed oil or dissolve in produced water. The relationship between the concentrations of selected compounds in stream prod 4 (underflow from hydrocyclone) and dispersed oil concentration is presented in Figure 5.7 to figure 5.9. The concentration of compounds in Stream Prod 4 was calculated using Equation 5.3

$$C_i = \frac{x_i m}{V_t} \tag{5.3}$$

Where C_i is the concentration of component *i*, x_i is the mass fraction of component i, *m* is the total mass flow rate of fluid (Prod 4), and V_t is the total volumetric flow rate of fluid (Prod 4).

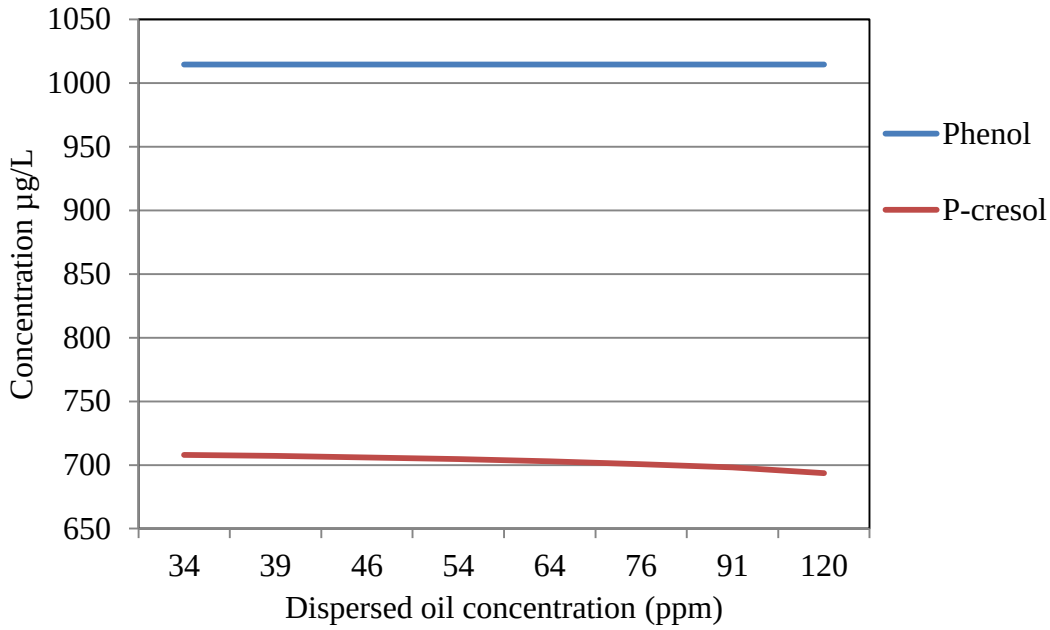

Figure 5.7: Concentration of phenol and p-cresol at varying concentration of dispersed oil in hydrocyclone underflow (prod 4)

The concentration of phenol remains the same as the dispersed oil concentration increases from 33 ppm to 120 ppm. Conventional produced water treatment system targets and reduces the oil in water however; a highly soluble compound such as phenol is not affected by the reduction in the concentration of oil in produced water. Similarly, the concentration of p-cresol shows no significant change as the dispersed oil concentration increases from 33 ppm to 120 ppm.

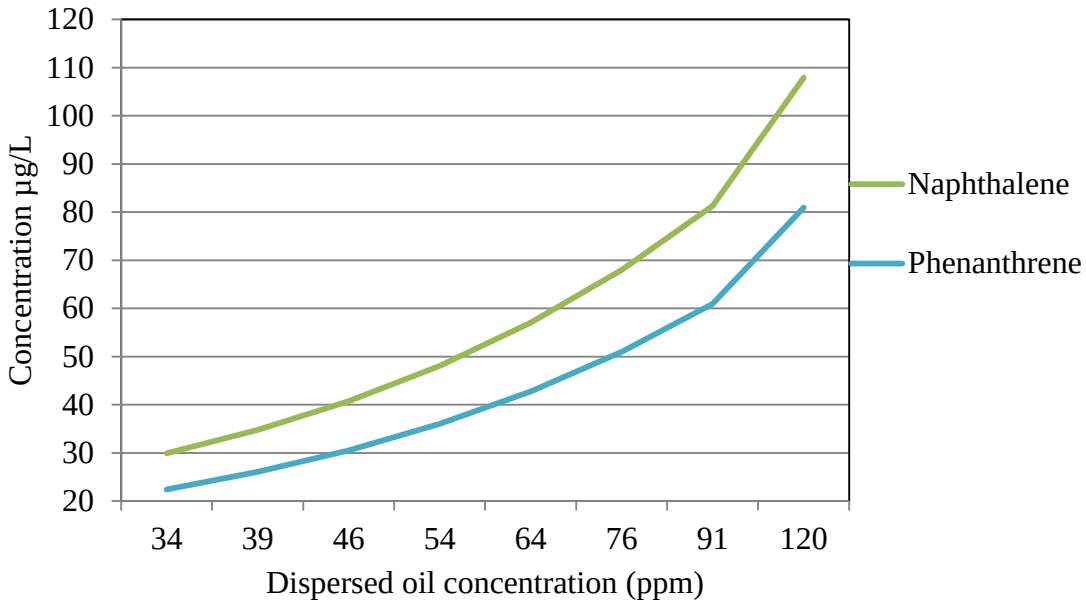

Figure 5.8: Concentration of naphthalene and phenanthrene at varying concentration of dispersed oil in hydrocyclone underflow (Prod 4)

The concentration of naphthalene and phenanthrene increases with increasing concentration of dispersed oil. A 72% decrease in dispersed oil concentration yields a 72.3% decrease in the concentration of naphthalene and phenanthrene. This indicates that there is a strong correlation between dispersed oil concentration and concentration of naphthalene and phenanthrene in produced water. Therefore, reduction in the concentration of dispersed oil has direct impact on the concentration of naphthalene and phenanthrene. Similar effect was observed for fluorene and pyrene as shown in figure 5.7.

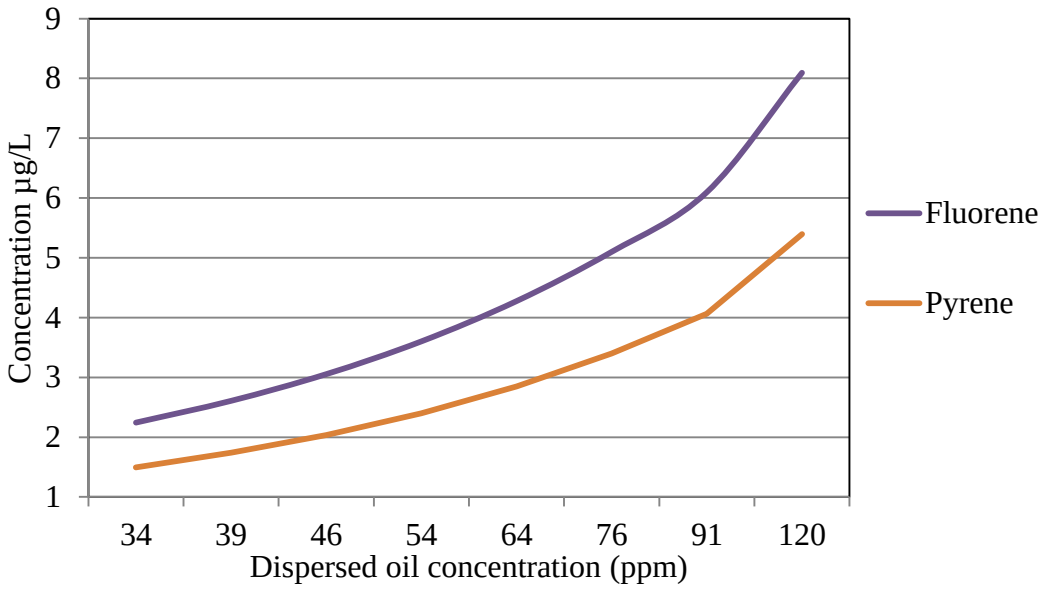

Figure 5.9: Concentration of fluorene and pyrene at varying concentration of dispersed oil in hydrocyclone underflow (Prod 4)

The concentration of fluorene and pyrene are strongly correlated to the concentration of dispersed oil in produced water Stream Prod 4 (underflow from the hydrocyclone)

All the PAHs studied shows direct correlation between the dispersed oil concentration and concentration of PAHs in Stream Prod 4. Therefore, hydrocyclone have great propensity to remove naphthalene, fluorene, phenanthrene, and pyrene from produced water by reducing concentration of dispersed oil.

5.6 Material balance

In order to determine the split of compounds in the separation equipment, component material balance was calculated for the hydrocyclone and the three phase separator. Results are presented in Tables 5.8 and 5.9.

Table 5.8: Component material balance in and out the hydrocyclone at 80 oC

Components	**prod 3**	**prod 4**	**oil**
Dispersed oil (ppm)	228	33.6	42.9E+2
H_2O (kg/h)	54.9E+3	52.4E+3	2.5E+3
Phenol (g/h)	54.9	52.4	2.50
P-cresol (g/h)	38.4	36.6	1.90
Naphthalene (g/h)	11	1.5	9.4
Fluorene (g/h)	0.8	0.1	0.7
Phenanthrene (g/h)	8.2	1.2	7.0
Pyrene (g/h)	0.6	0.1	0.5
Total mass flow (kg/h)	54.9E+3	52.4E+3	2.5E+3

At 80 ^{o}C about 95% of phenol and p-cresol in the feed stream (prod 3) into the hydrocyclone exits with prod 4 as underflow from the hydrocyclone. About 4.9% of p-cresol partitions into the oil rich overflow (oil). A reverse effect was observed for naphthalene, fluorene, phenanthrene, and pyrene. About 86% of these PAHs in stream prod 3 partitions into the oil rich overflow. The remaining 14% were associated with produced water in the underflow.

Table 5.9: Component material balance in and out of the hydrocyclone at 4 oC

Components	**prod 3**	**prod 4**	**oil**
Dispersed oil (ppm)	226.3	120.3	2840
H_2O (kg/h)	54.9E+3	52.8E+3	2.10E+3
Phenol (g/h)	54.9	52.8	2.10
P-cresol (g/h)	38.4	36.1	2.40
Naphthalene (g/h)	11	5.6	5.4
Fluorene (g/h)	0.8	0.4	0.4
Phenanthrene (g/h)	8.2	4.2	4.0
Pyrene (g/h)	0.6	0.3	0.3
Total mass flow (kg/h)	54.9E+3	52.8E+3	2.10E+3

For a feed stream at 4 ^{o}C into the hydrocyclone, the dispersed oil content in the underflow increases to 120 ppm and the oil removal efficiency of the hydrocyclone has reduced to 47%. Less than half of the dispersed oil is removed at 4 ^{o}C. About 49% of the PAHs flows into the oil rich overflow and 51% were associated with the hydrocyclone underflow (prod 4). Phenol and p-cresol were not impacted by the dispersed oil concentration with 95% still associated with prod 4. The mass flow rate of water in the overflow also decreases from 2500 kg/h at 80 ^{o}C to 2100 kg/h at 4 ^{o}C. This is likely as a result of higher density and viscosity of the fluid at low temperatures. Flow rate decreases with increasing viscosity as demonstrated by Poiseuille's law [55] presented in equation 5.4.

$$Q = \frac{\pi D^4 P}{128 \mu L} \tag{5.4}$$

Q is the volumetric flow rate, D is the diameter of pipe, P is pressure, μ is the viscosity of fluid, L is the pipe length.

Viscosity is inversely proportional to flow rate as shown in equation 5.4. Increase in viscosity will reduce the flow rate of fluid flow.

Table 5.10: Component material balance in and out of the three phase separator at 80 ^{o}C

Components	**Prod 4**	**prod 5**	**oil 2**
Dispersed oil (ppm)	33.6	2.10	8.60E+5
H_2O (kg/h)	52.4E+3	52.4E+3	1.50
Phenol (g/h)	52.4	52.4	1.00E-3
p-Cresol (g/h)	36.54	36.52	2.000E-2
Naphthalene (g/h)	1.6	0.0	1.6
Fluorene (g/h)	0.12	0.0	0.12
Phenanthrene (g/h)	1.16	0.0	1.16
Pyrene (g/h)	0.08	0.0	0.08

The mass flow of phenol and p-cresol in and out of three phase separator (represented by prod 4 and prod 5 respectively) remain unchanged with a negligible fraction partitioning into oil rich overflow stream oil 2. This is due to the high aqueous solubility of phenol and p-cresol. All the PAHs partition into the oil phase in Stream Oil 2. And the dispersed

oil concentration in prod 5 has been reduced from 33.6 ppm to 2.1 ppm. To remove highly soluble compounds such as phenol and p-cresol from produced water additional water treatment equipment will be required. Field trial of MPPE has proven to remove dissolved compounds such as phenol from produced water [8].

5.7 Comparison of Simulation result and experimental result

In order to provide a basis for comparison of simulation and experimental result, both simulated and experimental results were normalized. By normalization, the original data were mapped into a scale of one. Simulation results are represented with a grey shaded bar with no error term. Normalized simulation and experimental result for phenol is represented in Figure 5.9

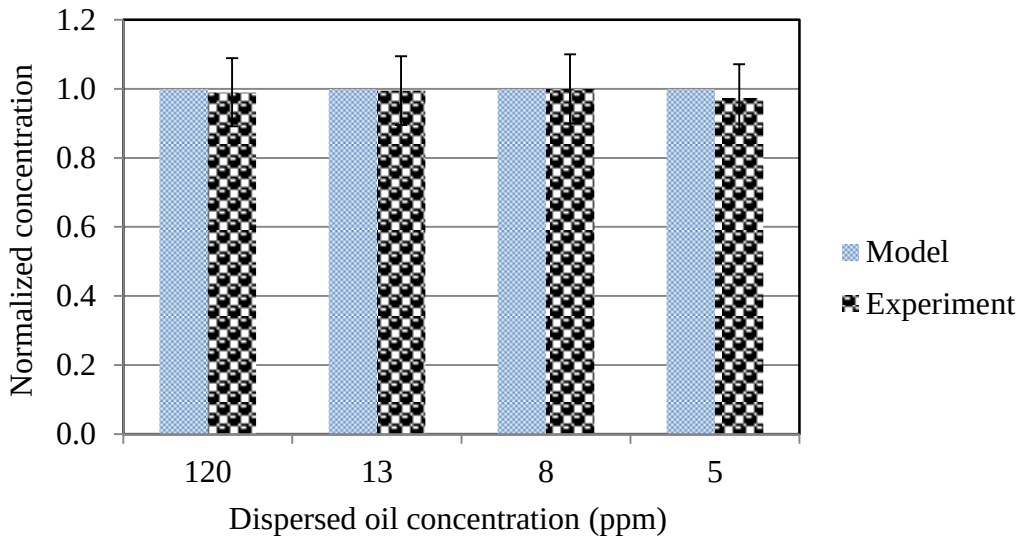

Figure 5.10: Comparison of normalized simulation and experimental result for phenol at varying concentration of dispersed oil

There is good agreement between model results and experiment result for phenol. Both model result and experiment result shows that the concentration of phenol is not dependent on the concentration of dispersed oil in produced water. The concentration of phenol in the water phase remains unchanged as the concentration of dispersed oil is reduced. It is important to remove phenol from produced water because it is toxic, carcinogenic, and mutagenic [8]. Phenol and alkylphenols play a significant role in the calculation of environmental impact factor (EIF). Phenols and other dissolved fractions in produced water can be removed by macro porous polymer extraction (MPPE) technology.

Figure 5.10 represent normalized and experimental result for p-cresol.

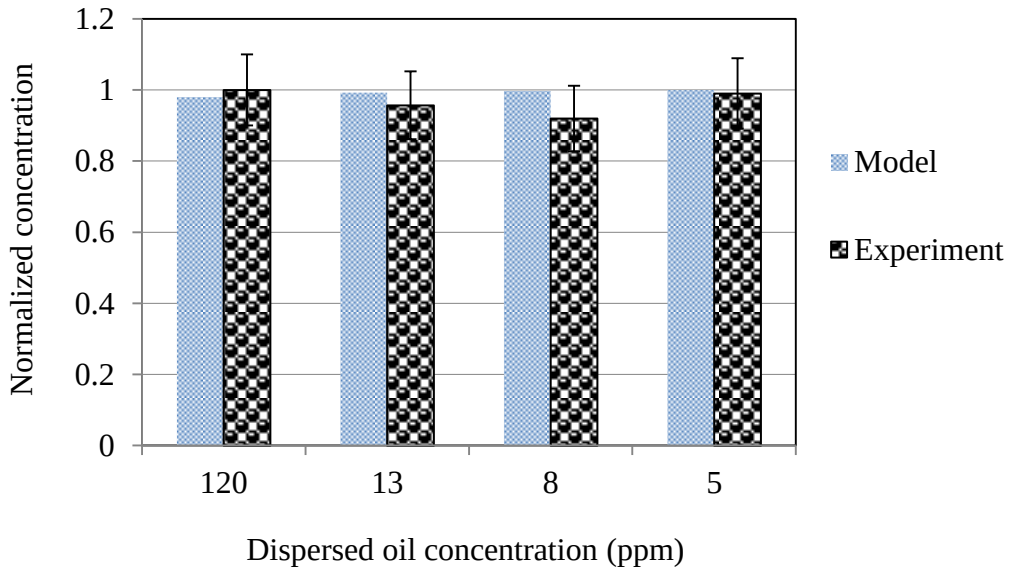

Figure 5.11: Comparison of normalized simulation and experimental result for p-cresol at varying concentration of dispersed oil

Simulation result for p-cresol shows that the concentration drop by 2% at 126 ppm dispersed oil. Similarly, experiment carried out at 50 ^{o}C and 66.8‰ salinity also shows that the concentration of p-cresol is not dependent on dispersed oil concentration. In the absence of experiment result a Simulation result can be used to predict the trend and partitioning behavior of p-cresol. This analysis shows the HYSYS simulation does reflect the trend for p-cresol. Figure 5.10 describe how simulation result compares to experimental result.

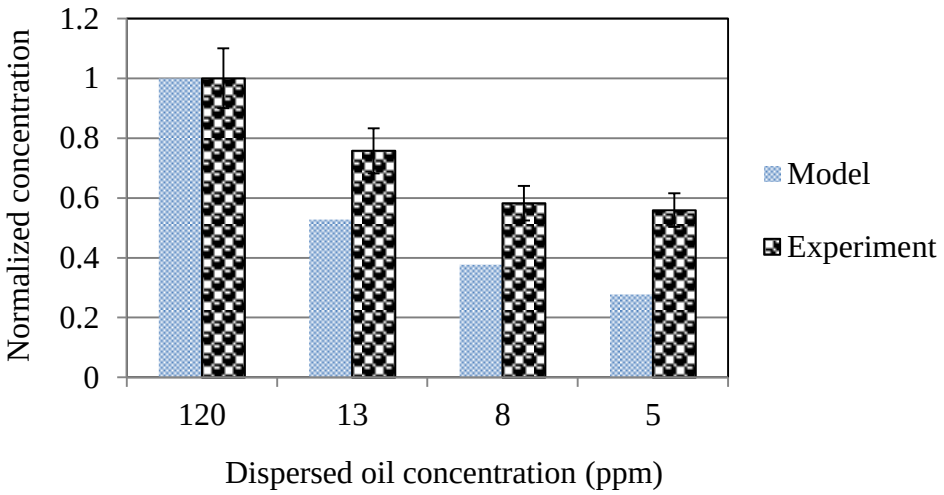

Figure 5.12: Comparison of normalized simulation and experimental result for naphthalene at varying concentration of dispersed oil

Results of experiment conducted at 26 ^{o}C and 66.8‰ shows similar trend with HYSYS simulation result. The prediction by HYSYS was considerably lower than observed concentration in the experiment conducted. It is likely that HYSYS may have over predicted the relationship between dispersed oil concentration and naphthalene. HYSYS predicted the same partitioning behavior for naphthalene and all the PAHs studied. This is at variance with experiment conducted which shows that solubility of naphthalene in

water play a significant role in the partitioning pattern. Experimental results shows that salinity have negligible effect on the partitioning pattern of phenols and p-cresol. Another factor that influences the composition and concentration of water soluble fraction in produced water is the water to oil ratio (WOR) [17]. This could be a factor in the concentration of naphthalene in the water phase due to its high aqueous solubility compared to other PAHs studied. The crude assay used to simulate produced water is not from the same oil field as the produced water sample used for the experiment. This could be a source of discrepancy in the composition and partitioning behavior of compounds under study in simulated produced water according to Shiu et al. (1990). However, both results show that the concentration of naphthalene decreases with decreasing concentration of dispersed oil.

Phenanthrene concentration decreases with decreasing concentration of dispersed oil. This is true for both simulated result and experimental result presented in figure 5.12.

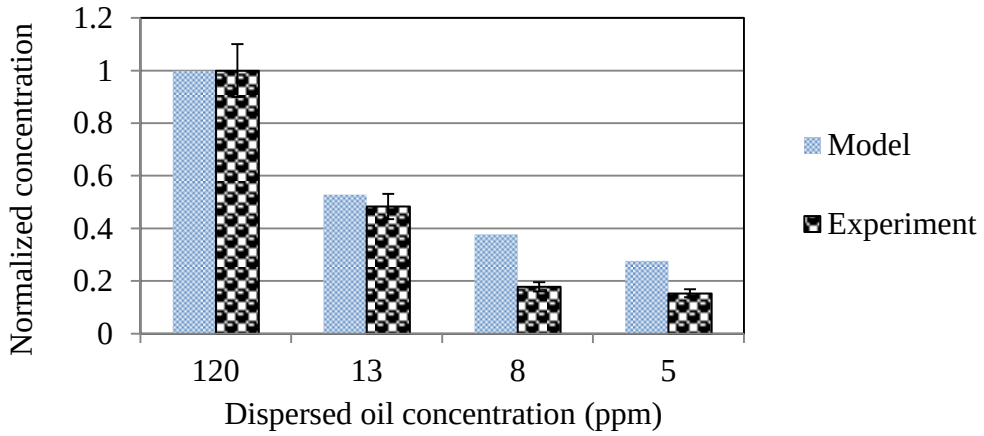

Figure 5.13: Comparison of normalized simulation and experimental result for phenanthrene at varying concentration of dispersed oil

The HYSYS simulation does not accurately predict experiment results at low dispersed oil concentrations. The disparity is likely due to reduced ability to accurately measure PAHs at low levels of dispersed oil. This is true for phenanthrene and all PAHs studied. However, it can be used to determine partitioning pattern of phenanthrene between the oil phase and water phase. Also HYSYS cannot be configured to take into consideration the effect of dissolved salts in produced water. Therefore effect of salinity on the partitioning pattern of PAHs is not covered by HYSYS simulation. The trend for both simulated result and experiment strongly shows that concentration of PAHs relates to the disperse oil concentration.

Simulation result closes matches experimental result at high concentration of disperse oil but significant differences exist at low disperse oil concentration for fluorene shown in figure 5.13

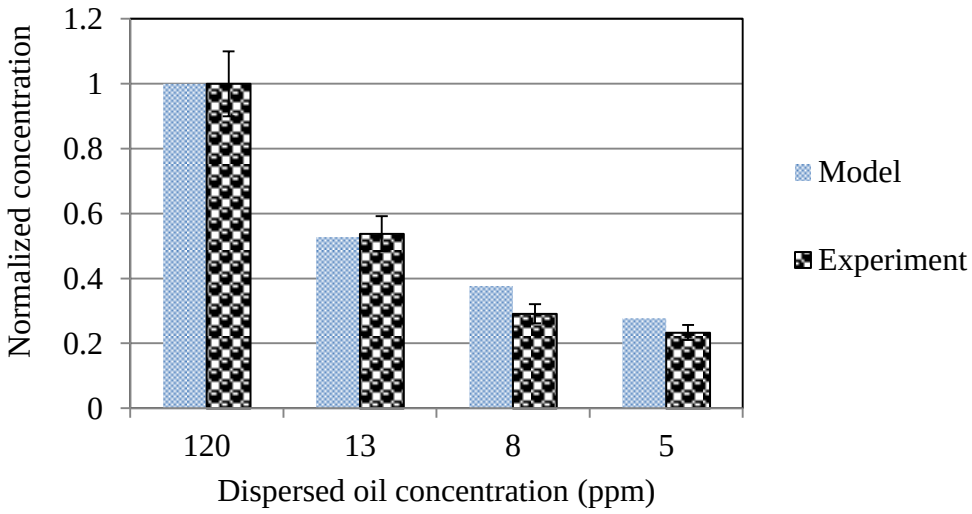

Figure 5.14: Comparison of normalized simulation and experimental result for fluorene at varying concentration of dispersed oil

The concentration of fluorene in the produced water is directly dependent on the concentration of dispersed oil. Reduction of dispersed oil concentration results in corresponding reduction in the concentration of fluorene. At low concentration of dispersed oil, the concentration of fluorene is close to detention limit of the analytical equipment used and measurement error increases close to detection limit of the analytical equipment. However, both experimental and simulation result clearly shows that fluorene concentration varies with concentration of dispersed oil in the water.

Figure 5.14 shows comparison of normalized model and experiment result for pyrene.

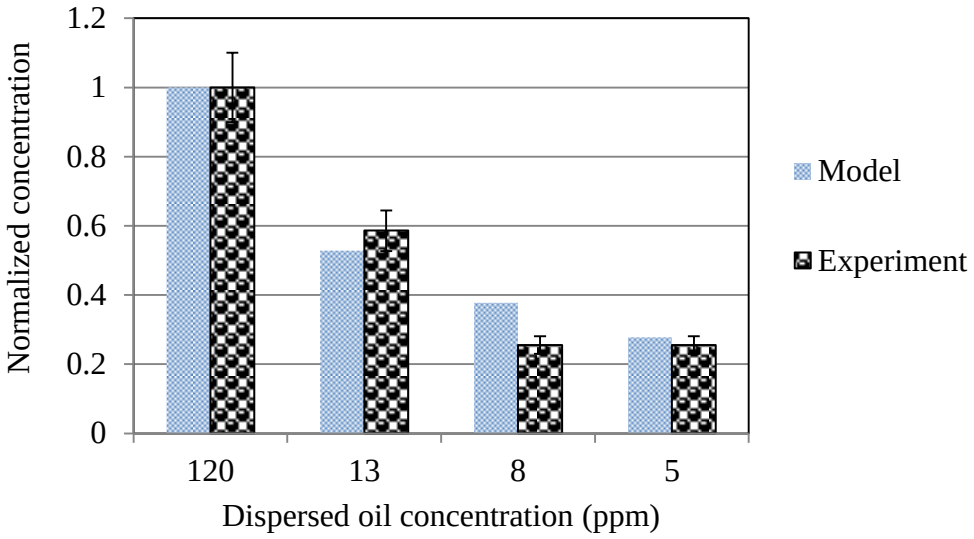

Figure 5.15: Comparison of normalized simulation and experimental result for pyrene at varying concentration of dispersed oil

Pyrene concentration in produced water is strongly dependent on the concentration of dispersed oil. Reduction in dispersed oil concentration also results in reduction in concentration of pyrene. This is in agreement with experimental result and is expected

due to the low water solubility of pyrene. The HYSYS simulation agrees with experimental data within experimental error except at low concentration of dispersed oil. This is due to inability to accurately measure concentration of PAHs at low concentration of dispersed oil.

Oil droplet distribution and feed temperature greatly influences the performance of hydrocyclones. At median oil droplet diameter (d50) of 35 μm the efficiency of hydrocyclone is 80%, oil separation efficiency drops to 28% at median oil droplet diameter of 12 μm. Studies show the hydrocyclone cannot separate oil droplet diameter below 10 μm from produced water [53, 56]. The activities upstream of the hydrocyclone inlet should be conditioned such that there will be little shearing of the fluids in the pipeline, pumps, valves, risers, and sampling point. Generally, low fluid velocity reduces possibility of oil droplet break up. Lager oil coalesces faster which in turn increases the rising velocity and aid its removal by hydrocyclone.

Increase in temperature increases the oil separation efficiency of hydrocyclone as shown in Figure 5.3. Increase in temperature reduces fluid viscosity thereby increasing the oil droplet rising velocity and subsequently increasing the oil-water separation efficiency of the hydrocyclone. Therefore in order to meet the oil in water discharge criteria of 30 ppm monthly average in Canada, the temperature of feed into the hydrocyclone should be maintained between 70 ^{o}C and 80 ^{o}C and activities upstream of hydrocyclone conditioned to reduce possible break up of oil droplet.

Hydrocyclone and other produced water treatment system that reduces the concentration of dispersed oil also have great propensity to remove PAHs from produced water. HYSYS simulation result shows that the concentration of PAHs in produced water is strongly related to the concentration of dispersed oil. However, phenol and p-cresol are not significantly impacted by reduction of dispersed oil in produced water and additional treatment equipment will be required to remove it from produced water. Macro porous polymer extraction has been proven to remove dissolved compounds (such as phenol) from produced water [29, 57]. However, this will require additional space and energy, a challenge in remote location. Although, full scientific proof (from ecological studies) of harm from produced water discharge into the marine is not available at the moment, but potential for harm has been established [56, 58, 59]. Therefore, the precautionary principle should be applied.

Chapter 6: Conclusion and Recommendations

6.1 Conclusions

This thesis presents the partitioning behavior of oil in produced water as a function of temperature and salinity to identify compounds of environmental concern. Settling experiments were conducted to determine the phase and partitioning behavior of seven selected compounds; phenol, p-cresol, 4-tert-butylphenol, naphthalene, phenanthrene, fluorene, and pyrene. A model was also developed using HYSYS simulation software to investigate the impact of oil droplet distribution and temperature on the efficiency of a typical produced water treatment system.

The experiment conducted clearly shows that dispersed oil rises to the surface with time and about 80% of the dispersed oil has risen to the surface after 12 h settling time. Equilibrium was attained at 48 h for all the experiments conducted. At 70 ^{o}C and 46.8‰ salinity the concentration of dispersed oil was lower than experiments conducted at low temperatures (4, 9.5, 15, 26 ^{o}C). This is likely as a result of increase in rising velocity of oil droplet as temperature increases. Dispersed oil concentration does not influence the concentration of phenol and p-cresol in the water phase. The partitioning pattern of phenol and p-cresol in produced water is not influenced by salinity and temperature within 4 ^{o}C and 26 ^{o}C. At higher temperatures the changes in the concentration of phenol and p-cresol observed was due to other external factors other than oil-water partitioning. Reduction in concentration observed at 70 ^{o}C is either due to volatilization or biodegradation. The partitioning pattern of 4-tert-butylphenol is similar to that of phenol

and p-cresol except that the concentration in produced water is considerably lower than concentration of phenol and p-cresol.

Generally, reduction in the concentration of dispersed also produces a corresponding reduction in the concentration of PAHs. There is a correlation between the dispersed oil concentration in produced water and PAHs studied. Naphthalene is partly dependent on the dispersed oil concentration in produced water. Although there is a reduction in the concentration of naphthalene it is not proportional to the concentration of dispersed oil. Similar effect was reported by Page et al (1999) and corroborated by Faksness et al. (2004). Increase in temperature tends to reduce the concentration of naphthalene in the water phase. This effect is attributed to naphthalene escaping from the matrix as temperature is raised or due to activities of thermophilic oil degrading bacteria previously found in neighboring field [35]. The effect of dissolved salt is not obvious, although the matrix becomes more turbid at 66.8‰ salinity and more dispersed oil was accommodated within the matrix.

There is a strong correlation between the concentration of dispersed oil and the concentrations of phenanthrene, fluorene, and pyrene in produced water. At low to ambient temperatures between 4^{o}C and 26 ^{o}C, equilibrium was reached after 48 h settling time. Approximately 8% of phenanthrene was left in the water phase. However 70 ^{o}C, 23% phenanthrene was retained in the water phase and equilibrium was achieved after 12 h even though the dispersed oil concentration in the water continues to decrease with time. It can be inferred that increase in temperature favors water solubility of PAHs while

increased in salinity favors partitioning of PAHs into the oil phase. More phenanthrene partition into the water phase as temperature increases. In summary, in order to detect PAHs in produced water, detection system should be deployed to target the oil phase, while to detect phenol, p-cresol, and 4-tert-butylphenol the detection mechanism should target the aqueous phase.

Results obtained from HYSYS simulation shows that oil droplet distribution and feed temperature greatly influences the performance of hydrocyclones. Increase in temperature increases the oil separation efficiency of hydrocyclone. Similarly, efficiency of hydrocyclones decreases as the oil droplet diameter reduces. And below mean oil droplet diameter of 10μm, the hydrocyclone does not have significant impact on oil removal from produced water.

Both experiment and simulation results shows that PAHs have direct correlation with dispersed concentration, therefore hydrocyclone and other produced water treatment system that reduces the concentration of dispersed oil also have great propensity to remove PAHs from produced water. Phenol and p-cresol are not significantly impacted by reduction of dispersed oil in produced water and additional treatment equipment will be required to remove it from produced water.

6.2 Recommendations for future work

1. This research should be expanded to include phase and partitioning behavior of BTEX, due to unavailability of purge and trap or head space facility, analysis of BTEX was not carried out. BTEX is known to be volatile; it will be interesting to

know how BTEX will partition between the water and oil, and/or water and air in the produced water settling experiments.

2. Ambiguity remains as to the possibility of activities petroleum degrading bacteria and micro-organism, therefore a full genome analysis of produced water should be done to determine the effect of microbial degradation
3. Further work should be done to simultaneously sample oil at the surface of the water to enable quantification of analytes in the oil at surface.
4. The model developed should be expanded to include compounds such BTEX and higher alkylated phenols.
5. One of the challenges faced in the course of experimentation is oil sticking to the sides of the aspirator bottle as a result of subsample collection and draw down. This may shift equilibrium condition. To overcome this, four sets of homogenize sample should be used. This way, each bottle is to be sampled once and hence likely error that may be introduced as a result of draw down will be eliminated.
6. A dynamic modeling of the produced water treatment system should be done in order to fully mimic a produced water treatment plant running conditions. Also other factors (pressure drop, fluid flow rate) that influence the performance of the produced water treatment plant should be investigated.
7. Mathematical calculation of the partition coefficient to be done

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